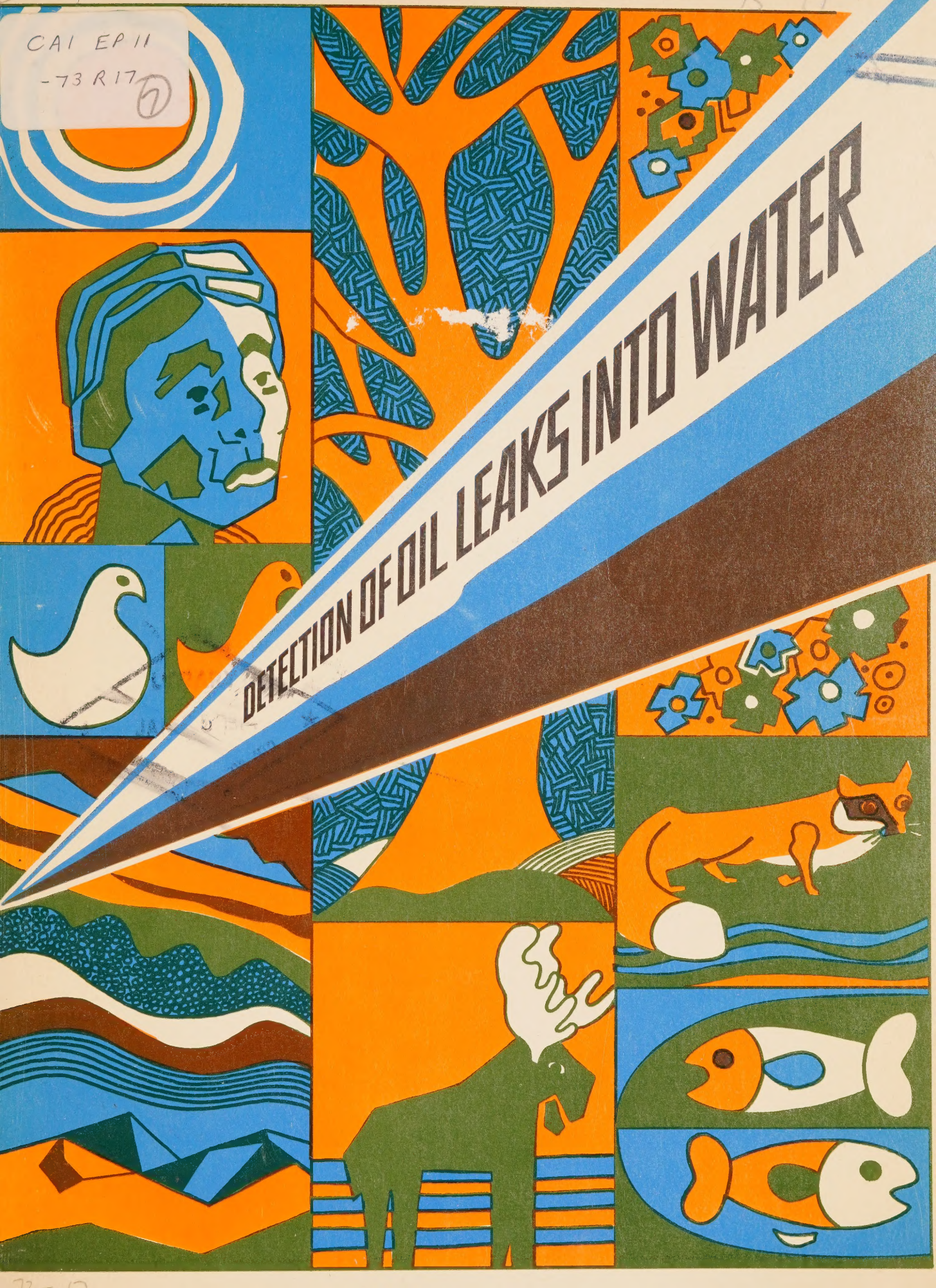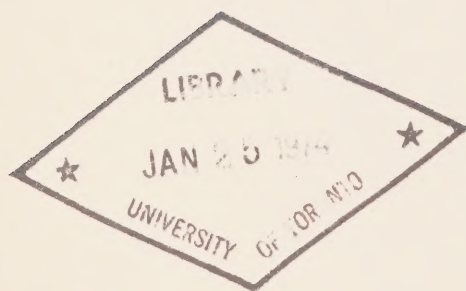# DETECTION OF OIL LEAKS INTO WATER

FEASIBILITY STUDY ON A METHOD FOR THE DETECTION OF

OIL LEAKS INTO WATER

by

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1.   Summary

A variety of laboratory simulations in the current feasibility study showed that oil escaping from a buried pipeline at a river crossing would introduce readily detected fluorescent hydrocarbons to the water at that point. Such hydrocarbons would be detectable in the water down-stream from that point despite the presence of coloured organic matter and suspended mineral matter. Fluorescent substances would persist for hours even though the more volatile components would evaporate quickly.

While the monitoring of flowing streams would evidently provide a possible method for detecting pipeline leaks at river crossings, a second method emerged in the course of the study as a more promising monitoring system. The new method depends on monitoring water withdrawn not from the flowing stream but from the river bed immediately over the buried pipeline. Again, in simulation studies, escaping oil introduced the same fluorescent hydrocarbons into the water as before and they were detected by the same instrumentation. Several advantages for such a method appeared. One was that the fluorescent matter moved ahead of the escaping oil. Thus a fluorescent halo developed that was detectable by river-bed monitoring before the oil reached the water in the flowing stream. Another advantage was that very small leaks would be detectable since the studies showed that the overlying sand appeared to act as a collector around which the halo built up. A further major advantage was that the sampling device would be well protected from damage in the stream caused by ice scour and the passage of solid bodies such as timbers and rocks.

The results of the current study, in particular those dealing

with river-bed sampling, indicate that the use of fluorescence instrumentation

for monitoring water for oil leaking from buried pipelines is a very

promising approach, one that should be developed without delay. It is

recommended therefore that a group of development studies be undertaken

in the coming years to provide for such development. Such studies would

call for the design, construction and testing of field instrumentation,

as well as for similar development of sampling units for river-bed

application. To complete the study, provision would also be made for

interfacing with telemetry systems. A cost/benefit analysis would guide

the overall undertaking.

2. Objectives

With the completion of an initial feasibility study for fluorescence detection of oil in water (1), the basic objective of the current project was to more exhaustively develop the principles of fluorescence detection with experiments simulating the key aspects of a field application. With this approach it could then be determined how well the principles of fluorescence detection were suited to northern environments.

A number of problems needed to be resolved before the principles of fluorescence detection could be adopted. These included: the effects of near-freezing water temperatures on the fluorescence signal; the destruction of monitoring equipment by ice flows or flood; the placement of the detection unit to yield optimum response; interference in signal of oil-derived fluorescent compounds by various substances in the natural waters; finally problems of increasing the sensitivity of the instrumentation without loss of simplicity. These problems led to a structuring of the work program as follows:

    instrument design

    temperature effects

    river water properties

    location of the detection system.

In the course of the work sufficient data were obtained in all sections to establish the feasibility of the method leading to recommendations for further developmental research, including prototype design and construction along with field testing.

3.   Instrument Design

Because of the need for a rugged and durable fluorescence instrument, improvements to the Turner model III fluorometer were constantly being adopted during the course of operations. Consequently, because of the mechanics of improving the performance of the model III instrument during the first few months of operation the Turner model 210 (double monochrometer) was used in the interim. Alterations to this instrument included changing the cell compartment to accommodate a flow through quartz cell. Thus, results from sections 4. and 8. were obtained primarily with the Turner model 210. Fortunately, the improvements to the model III left the two instruments with remarkably similar performance, thus allowing some direct comparison of results. In addition, the model III was now capable of greater sensitivity than the model 210 with certain electronic modifications using a variable input recorder. The improvements in design of the Turner III fluorometer are discussed in the following section.

3.1 Design Improvements

Two main areas of interest for improvements were the optical system and amplification of the instrument output using a more sensitive and versatile recorder.

Three possible methods for improving the optical system were considered. A more intense light source or more efficient primary and secondary filters would all contribute to a more responsive instrument. Replacement of the primary filter appeared to be the most productive approach. The replacement filter was a coated reflecting ultraviolet filter with performance specifications as illustrated in figure 1. This filter had a 26%

transmission at 253.5 nm and a half band width of 13.6 nm. Thus it had
a high transmission of pure mercury light. This particular quality was
necessary to eliminate the high background caused by light transmitted
at wavelengths greater than 300 nm, particulary in the region of 335 nm where
the fluorescence of aromatic hydrocarbons was to be detected.

The instrument output was amplified through the use of a model
7127A Hewlett Packard strip chart recorder with model 17501A range
module. With an instrument signal output of 10 mv a chart recording of
5 mv full scale doubled the sensitivity of the instrument. This was
found satisfactory since the signal to noise ratio was low (i.e. 10:1).

3.2 Results of Design Improvements

With the addition of the excitation filter without the new
recorder, figure 2 shows the comparison between the Turner 210 and 111.
The signals from the Turner 111 were approximately 60% those of the
Turner 210. Illustrated in figure 3 is the effect of recording Atkinson
Point signals at both the 2 and 5 mv levels. The increase in noise at
the 2 mv level can be obviated with a suitable electronic pen damp.

Thus, in general, two areas of instrumentation were readily
upgraded. Additional improvements are still possible should they be
required.

4. Temperature Effects

A complete temperature study involving contacting Atkinson Point and Prudhoe Bay oils with near freezing water flow systems became necessary to determine if very low stream temperatures might seriously hinder or prevent the detection of an oil leak by:

    (a) limiting the solubility of fluorescent hydrocarbons in water.

    (b) limiting the rate of extraction of the fluorescent material from the oil by the flowing water.

    (c) altering the fluorescent characteristics of the dissolved hydrocarbons.

For practical purposes, the primary objective of this study area involved measuring the signal at temperatures very close to $0^{\circ}C$. Defining which parameters limit the signal was of secondary importance.

4.1 Experimental Procedure

The dynamic system employed the same flow cell as was used in the feasibility study (1). This consisted of a horizontal glass cylinder about 15 cm long and 5 cm in diameter (figure 4). The trapped air volume above the flowing water was 20% - 25% of total volume giving an exposed surface area of about 30 cm^2. The water flow rates were consistently 26 liters/hr $\pm$ 1 liter/hr. This slower than usual flow rate was chosen to facilitate cooling the flowing water. Oil was introduced into the flowing system by a single injection through a septum. Care was taken to layer it onto the surface of the water in the cell.

Considering 1 hour of water flow, the size of oil injection ranged from 0.026 ml $\pm$ 0.003 ml (designated 1 ppm/hr) to 2.6 ml $\pm$ 0.2 ml (designated 100 ppm/hr).

Studies were carried out at temperatures of 2°C, 10°C and 19°C. Temperature of the water was controlled by an ice bath and a Lauda K-4/R cooling bath. Water leaving the cell was sampled by leading a portion of the stream into a 100 mm quartz flow cell modified to adapt to the Turner 210 spectrofluorometer. The monochrometers were locked at 280 - 335 nm (the oil fluorescence maxima) and time-temperature tests were carried out.

To eliminate problems of condensation on the quartz cell surface, the entire apparatus was placed in a cold room operating at temperatures at or below the water temperature.

4.2 Results of Temperature Effect

Detection levels were obtained for Atkinson Point and Prudhoe Bay oils, at temperatures of 2°C, 10°C and 19°C for two levels of oil concentration. The major parameters involved were oil concentration and water temperature. Measurements were made of the intensity and duration of the fluorescence signal.

4.2.1 Oil Concentration

The results for Prudhoe Bay and Atkinson Point oils differed mainly in signal intensity. For example, using a flow rate of 26 liters/hr and oil additions of 0.026 ml and 2.6 ml, Atkinson Point displayed signals of 12 and 17 units respectively for the two concentrations of oil.

Correspondingly, Prudhoe Bay exhibited signals of 34 and 38 units for the same concentrations.

After 1 hour of contact the signal output for both oils decreased to half for the low concentrations (0.026 ml oil) and 19°C, while the signals for the flow system operated at the high concentrations remained steady. This suggests that the water for lower oil concentration lost about half of its aromatic compounds while the water for the higher oil concentration remained saturated. Tables 1 and 2 illustrate initial responses for Atkinson Point and Prudhoe Bay oils respectively. The increased oil concentration (100 ppm/hr) indicated a greater initial response for each oil, and as indicated above, this response remained at a stable level while the response for the lower concentration decreased after 1 hour. Figure 5 shows the effect of changing oil concentrations as well as the overall effect of the temperature changes for both oils.

4.2.2 Water Temperature

For the same flow conditions as in 4.2.1, the signal for Atkinson Point oil increased from 6 to 12 units as a result of increasing the temperature from 2°C to 19°C. Similarly Prudhoe Bay yielded increases of 18 to 34 units over the same water temperature range (tables 1 and 2).

Analysis of signal durations for both oils indicates a longer retention time of signal intensity at low temperatures as compared with tests at 19°C. This effect is shown in figures 6 and 7 where tests were run at three temperatures and a common oil concentration. For both oils used, the test run at 19°C showed the greatest drop in response after

Table 1

Temperature Effect for Atkinson Pt.

Temp. °C	1 ppm/hr			100 ppm/hr		
	Initial signal	Flow (1/hr)	Rm. Temp. (°C)	Initial signal	Flow (1/hr)	Rm. Temp. (°C)
19°	12	25	22°	17	25	22°
10°	6	27	9°	9	27	7°
2°	6.5	26	2.5°	10	27	2°

Table 2

Temperature Effect for Prudhoe Bay

Temp. °C	1 ppm/hr			100 ppm/hr		
	Initial signal	Flow (1/hr)	Rm. Temp. (°C)	Initial signal	Flow (1/hr)	Rm. Temp. (°C)
19°	34	25	22°	38	25	22°
10°	18	27	7°	29	26	8°
2°	18	28	3°	29	26	1°

30 to 60 minutes, while the tests run at 2°C and 10°C yielded a more uniform signal over the same time period.

Results for Atkinson Point in figure 7 indicate that the initial signal intensity was halved after only 5 minutes of monitoring at all temperatures tested. The single bulk injections of this particular oil were the cause of this phenomenon. In subsequent sections the continuous flow of oil in the completely dynamic system yielded the predicted steadily increasing signal, regardless of the oil type used. Thus, the sudden decreases in fluorescence response may be eliminated by using a more practical arrangement of apparatus.

4.3 Summary of Temperature Effect

The experimental data obtained through the study of the temperature effect lead to a number of basic observations:

1. Atkinson Point and Prudhoe Bay are both detectable to temperatures as low as 2°C.

2. Atkinson Point appears to be the more difficult oil to detect because of its lower fluorescence response and shorter retention time of peak response.

3. Cold water temperatures lengthen the duration of peak response, as compared to temperatures of 19°C.

4. Cold water temperatures have the effect of lowering the fluorescence response by 1/4 to 1/2 of the corresponding values monitored at 19°C.

5. Fluorescence responses for Atkinson Point were consistently 1/2 to 1/3 of the values obtained for Prudhoe Bay oil.

5. River Water Properties

When originally presented in the proposal, this project called
for a downstream water sampling method for detecting oil-derived
fluorescent hydrocarbons. Later, it developed that a more satisfactory
method of sampling was a method based on sampling directly from the river bed,
thus eliminating any problems of river water properties. Nevertheless, tests
and observations were made in light of the following parameters:

1. quenching of the fluorescence signal by dissolved coloured
   material in the water.

2. interference by the natural fluorescence of dissolved material
   in the river or by fluorescent particles.

3. adsorption of the oil-derived fluorescent compounds by
   suspended organic matter or clay minerals.

4. interference in the fluorescence signal as a result of light
   scatter caused by turbid solutions.

5. loss of the dissolved fluorescent compounds either to the
   atmosphere or by chemical processes.

5.1 Experimental Methods and Results

Samples of five river waters from the Mackenzie River drainage
basin were obtained and used in resolving the foregoing statements.
Under various conditions the waters were first tested as a blank and
then monitored with added known fluorescent material (1 ul/ml
methyl naphthalene). Data for the river samples are given in table 3.
A breakdown of methods and results for individual parameters follows.

Table 3

Data for River Waters

Sample	Location	Solids Content mg/1
d3370	Keele River	2420
d3373	Willow Lake River	136
d4460	Arctic Red River at Martin House	170
d4461	Arctic Red River at Arctic Red	177
d4462	Mackenzie River below Arctic Red River	750

Table 4

Quenching of Fluorescence Signal
with Humic Acid

Sample	With Humic Acid		Without Humic Acid	
	blank	1 ul/ml methyl napthalene	blank	1 ul/ml methyl napthalene
d4460	0	7	0	100 +
d3370	0	3	0	73

5.1.1 Quenching

        To resolve part (1) of section 5, a quantity of humic acid was
dissolved in river samples d4460 and d3370 to simulate additional
dissolved coloured material that might be present in tributary streams from
muskeg areas in the water; samples with and without 1 ul/ml methyl
naphthalene were monitored.

        The fluorescence signal was quenched to a large degree by the
presence of the humic acid in the water, as shown in table 4. As a
quantitative value describing the degree of colouring, figure 8
illustrates a per cent transmission curve of sample d4460 with and without
humic acid. The transmission of light dropped from 50% to zero, thus
explaining the low fluorescence signal of the sample containing humic
acid.

5.1.2 Interference by Natural Fluorescence

        This parameter was analyzed by monitoring the river waters for
their fluorescence before and after the addition of 1 ul/ml methyl
naphthalene. The difference in signal gave quantitative values for
interference by natural fluorescence. Figure 9 illustrates that no
interference in signal by natural fluorescence occurred. At the
wavelengths of interest (280/335 nm) scan (1) shows a blank while scan
(2) illustrates the effect of adding 1 ul/ml methyl naphthalene. All
five waters gave the same results.

5.1.3 Adsorption by Organic Matter
        The procedures involved allowing two samples of each river

water, one containing 1 ul/ml methyl naphthalene and the other "as received", to settle for 24 hours before examination for fluorescence. If the fluorescence in the "loaded" sample persisted it was concluded that there was no adsorption of the fluorescent compounds by the settled organic matter and clay minerals. Scan (4) in figure 10 remained high in fluorescence response indicating no adsorption of the oil-derived fluorescent compounds. These results are typical for all five waters tested.

5.1.4 Light Scatter

Resolving this parameter involved monitoring the river water as a blank to determine whether the instrument was capable of transmitting light through the turbid sample. All five river waters provided positive readings using the Turner III. Thus the turbidity of such samples does not present a problem of interference in the fluorescence signal, although it does decrease the intensity. The high intensity of the settled sample (scan (4), figure 10) compared to the lower intensity "as received" sample (scan (2), figure 9) illustrates the effect of turbidity on the fluorescence. However both scans show sufficient fluorescence response for detection.

5.1.5 "Weathering" of Oil in Water Systems

In an earlier study of the identity of the water soluble fluorescent constituents of crude oil and the effects of simulated weathering (1), it was shown that: (a) the fluorescent water soluble compounds were mainly naphthalene and methyl naphthalenes, (b) in a simulated oil spill individual fluorescent

compounds were dissolved by the water and subsequently lost to the atmosphere at rates depending upon their molecular weight and vapor pressures, (c) differing rates of exchange of the various compounds between oil, water and air resulted in changes in the composition of water-dissolved hydrocarbons and consequently changes in the wavelength of the fluorescence maxima, and (d) even under conditions favorable for the dissolution of the fluorescent hydrocarbons in water about 50 percent was lost to the atmosphere within 13 hr.

In the present contract two further experiments were conducted to evaluate the effect of (a) wind and (b) wind with turbulence, upon the build up and subsequent decline of fluorescence in water systems in contact with crude oil. In both experiments a glass cylinder 28.5 cm in diameter was filled to near capacity with 19 liters of water containing 5.26 g. of sodium bicarbonate (for pH control). The container was placed on a large magnetic stirrer and fitted with a small glass tube to allow sampling from the bottom. A magnetic stirring bar was added and 10 ml. of Prudhoe Bay oil was poured on the surface. Air from a small fan produced a wind of 5 m.p.h. at the surface of the water as measured with an anemometer. In the first experiment designed to study the effect of wind, the water was stirred slowly so that a small vortex appeared but no globules of oil were dispersed in the water. In the second experiment, involving both wind and turbulence, the water was violently agitated by air introduced via a tube with a coarse glass frit at the rate of about 3 liters per minute. This resulted in vigorous mixing of the water, dispersion of oil throughout the water and foaming of the oil at the surface. Water from the bottom of the vessel was

sampled over a period of four days and the fluorescence measured with excitation at 280 namometers.

In the wind experiment, during the first four hours of mixing, the oil circulated on the water surface in one or more pools covering less than 20% of the surface area. During this period the water exhibited only slight fluorescence. After about four hours the oil spread completely over the surface in a uniform layer and the fluorescence of the water increased until a maximum was reached after 20 hours. This level of fluorescence was maintained for the next 30 hours after which there was a slow decline. Fluorescence during the 20 to 50 hour maximum was equivalent to approximately 35 mg/l dissolved hydrocarbons in the water. This compares with 186 mg/l in an experiment which had twice as much oil and in which there was no wind. Thus although the effect of wind was not precisely measured it is estimated that the 5 m.p.h. wind brought about a 60% reduction in the maximum amount of fluorescence appearing in the water. The rapid build-up of fluorescence in the water once the surface was oil covered completely indicated that losses of low molecular weight fluorescent hydrocarbons, primarily naphthalene, were rapid at the water-air interface but were retarded by the oil layer. The fact that the fluorescence once attained persisted and was only slightly reduced after 3 1/2 days showed that the wind caused large losses of the lower molecular weight compounds but the higher molecular weight compounds were not so greatly affected. The net effect of the 5 m.p.h. wind was to reduce the fluorescence signal but not by any means to eliminate it nor to greatly alter its persistence.

In the experiment involving both wind and turbulence, the

violent mixing and dispersion of oil droplets caused a rapid introduction
of fluorescence to the water. After only one hour the water contained
34 mg/l fluorescent hydrocarbons or about the same level as was attained
after 20 hours in the previous experiment. The fluorescence reached a
maximum by the second hour (39 mg/l) and thereafter declined at a
slow rate until the water contained only 23 mg/l after 4 days. Thus the
violent mixing caused by aeration simply accelerated the rate of
fluorescence build-up but did not substantially alter the persistence of
the fluorescence. Results from this and the previous experiment indicate
that even under the most turbulent conditions in the river systems the
fluorescence signal from dissolved hydrocarbons would persist but perhaps at
a lower level than under quiescent conditions.

5.2 Summary of Water Properties

It may be generally concluded that interference effects attributable
to the water properties do not greatly limit or obscure the fluorescence
signal. This conclusion is perhaps of minor importance since the prime
area for sampling now appears to lie in the river bed itself. For this
reason, the relevant procedures and results have been reported only briefly.

6. Location of the Detection System

To study the question of where best to locate the detection device in the river system, scale models of rivers and river beds were constructed. Laboratory tests using these models were carried out to resolve the best placement of the detector in terms of peak fluorescence response. Problems of hazardous placement caused by ice flows, etc., were also considered as factors in determining the most suitable location of the detector. For these reasons, two different sampling techniques were explored in great detail. The two methods were:

1. downstream sampling in water

2. river bed sampling at source of oil leak

The latter method would locate the sampling device in the river bed to monitor ground water immediately above and slightly down-stream from the buried pipeline. Each of the variables involved in the design location of the leak detector was isolated and blocks of experimental data were obtained to determine the effect of the various parameters through laboratory simulations. The river bed sampling method proved more plausible; therefore, more emphasis was placed on this area of experimentation. A problem resulting from the river bed tests was that of determining the extent of lateral oil movement through the sand prior to vertical penetration to the sand water interface.

6.1 Analytical Methods

In the following sub-sections general information is given as to the methods of analysis for the location of the detector system. More detailed procedures are located in the appendices under the appropriate headings of subsequent sections.

6.1.1 The River Model

To study downstream sampling and river bed sampling on a laboratory level, a scale river model was built, as shown in photographs 1 and 2. This model was rectilinear and measured 16 ft. long by 15 in. wide and 8 in. deep with an inlet and outlet reservoir to supply and drain the water. The water flow rate was adjustable to 3 levels, namely 0.5 ft^3/min, 1.0 ft^3/min and 1.5 ft^3/min. Simulating the leaking buried pipeline was a series of 5 injection parts equally spaced across the width of the model 2 1/2 ft. downstream from the inlet reservoir. Access to the river bottom through the injection ports was provided by an oil filled syringe mounted on a model 355 Sage syringe pump capable of supplying oil flow at rates over a range of about 10^{-5} to 150 ml/min. The sampling water was drawn by vacuum through a quartz flow cell into a series of 21 liter pots. An in-line valve controlled the sampling flow rate.

6.1.2 The Instrumentation

The recorded results were obtained through the use of a Turner 210 spectrofluorometer. This was the same double monochrometer system used in the feasibility study but modified to handle a quartz flow-through cell. Midway through the experiments the Turner 111 fluorometer, with improved optical system coupled with a Hewlett Packard model 7127A strip chart recorder and a 17501A range module, was incorporated into the apparatus (details of this instrument and its improvements are found under 3. Instrument Design). These two instruments generated enough data to resolve the effects of the variables listed under the headings in subsequent sections.

6.2 Summary of Detector Location System

Using the sampling methods, models and detection equipment described previously, the problems of locating the detector were systematically resolved. Because of natural hazards such as ice flows and flood it was necessary to explore various methods of water sampling. For this reason river bed sampling was tried and proven to be a more reliable method of monitoring than downstream water sampling. Thus the problems of detector location were centered on this new method of sampling. The following sections therefore, are sequenced to give the reader a complete view of detector location work by analyzing first the downstream water sampling method; second, the river bed sampling method; and third, the lateral movement of oil in a sand-water medium.

7. Downstream Sampling in Water

The parameters considered in this block of experiments were:

rate of oil injection

rate of water flow

distance downstream from oil source to sampler

location of sampler across width of model

depth below surface of sampling point

A multidimensional grid of all five variables would provide complete knowledge of oil detection in the model. Because these data would vary for different streams or models, the object was to analyze only key sectors of the grid in terms of major changes in signal stability and intensity caused by any one of the parameters. Explanation of procedures for analyzing each of these parameters can be located in Appendix A.

7.1 Results of Downsteam Sampling

The data generated in this section resulted primarily from the use of Prudhoe Bay oil. In order to observe and compare relative intensities of two different oils, limited corresponding data were obtained for Atkinson Point as well. It was generally found that the fluorescent signal produced at various distances downstream from the leak source showed inconsistent relationships, compared one to another, when monitored in light of the variables considered. Thus, the downstream water sampling method proved to be deficient in terms of stability and consistency.

7.1.1 Oil-Water Ratios

Selection of the oil-water ratios was possible in either of two ways; by changing the water flow rate with a constant oil flow rate or by varying the oil flow rate while keeping the water flow constant. The overall effect was the same. As shown in Appendix A, section 6, the oil-water ratios varied between 1/60000 to 1/1,200,000. The small ratios, achieved by increasing the water flow, produced a "washed out" (i.e. less intense) but more stable signal than the large ratios. This fact was emphasize when sampling took place closer to the source (i.e. 1 ft. instead of 8 ft. downstream) as shown in figure 11. The signal pulses in this figure were due to the intermittent presence of highly concentrated fluorescent "pools" resulting from oil droplets bursting at the water surface. As the "pools" had the chance to mix downstream or be washed away by rapid water flows, they tended to increase the stability and decrease the intensity of signal respectively. The general result then, was a pulsating low-intensity signal which stabilized but decreased in intensity as the oil-water ratio became smaller.

7.1.2 Distance Downstream from Source

Sampling at two arbitrary locations of 1 ft. and 8 ft. downstream from the oil source produced little change in the signal output. With more time for mixing and dispersion of fluorescent compounds to occur at the 8 ft distance, it was not surprising to find the signal more uniform at that point. For a particular set of flow and sampling conditions, figure 12 indicates this uniformity at 8 ft. as well as a similar average

intensity for the two sampling positions. When another set of flow and
sampling conditions was employed and again a comparison drawn between two
sampling distances, the same conclusions could not be reached. Under some
conditions, a change in flow rate caused a severe "wash out" of signal
at one location but not at the other, or a change in location sometimes
provided an improved response at both locations. Thus, resolving one
variable in terms of all other parameters became quite complex. Note
that the short burst of high intensity fluorescence at 33 min. and
8 ft. in figure 12 was due to the passing of a long oil plume down the
center of the stream (see photograph 2).

7.1.3 Location of Sampler Across Width of Model

Figures 13 and 14 show the effect of sampling at various points
across the stream. Figure 13 shows data for sampling at a point 8 ft.
downstream. It indicates a signal at lateral points (1) and (6) with
intensities 6 to 8 times greater than that at the center point (C).
Figure 14 gives data for sampling at a downstream distance of 1 ft. and it
indicates a signal strength at point (1) twice as great as that at the
center point (C); the observed signal at (1) was 18 to 22 units. Thus,
there was a suggestion that fluorescent material tended to congregate near
the "banks" of the river rather than at the center. This was probably
related to the flow patterns in this particular model in which higher
stream flow occurred in the center with slow movement near the "bank".
It should be noted that water from near the edge of the stream (along
the "bank") gave the highest signal of all downstream water sampling
experiments.

7.1.4 Sampling Depth Below Water Surface

Vividly shown in figures 13 and 15 is the effect of changing sampling depth below the water surface. The signal dropped to nearly 1/4 the near-surface level with an increase in sampling depth of 1.5 in. Shown on a small scale in figure 16 is the effect of increasing the sampling depth in smaller increments, the decrease in signal being not as significant but reinforcing the fact that best results occur when sampling takes place near the water surface. In addition to illustrating the effect of sampling depth, figure 13 also indicates water flow rate and cross-stream effects within the same test. The entire experiment is a good overall description of the effects of these three parameters.

7.1.5 Atkinson Point and Prudhoe Bay Comparison

The results in figure 17 confirm earlier observations that Prudhoe Bay oil is more easily detected than Atkinson Point oil in downstream detection systems. The results shown are for the most intense signals produced under any of the conditions tested, including an ideal oil-water ratio for detection. Other conditions yielded results for Atkinson Point only one unit above the zero base line.

7.1.6 Oil Plume Dispersion

Studies by Fisher (2 and 3) show development of methods for determining longitudinal mixing coefficients in river channels. These methods were determined using rhodamine B or rhodamine WT dye tracer solutions in field experiments in specific U.S. rivers. Prediction of a longitudinal dispersion coefficient for a natural stream requires field measurement of channel geometry, cross-sectional distribution of velocity and a calculated

value of the transverse mixing coefficient (2). As a tracer dye moves
downstream its progressive transverse and longitudinal location is recorded.
These data along with a number of derived equations for diffusion and mixing
in natural streams are used to calculate the longitudinal dispersion
coefficient for individual channels. The accuracy of the dispersion
coefficient depends partially on the size of the channel, (more difficult
to calculate coefficients for wide meandering channels) the stream's
meandering characteristics and the abundance of stagnant pockets or pools
along either bank, (stagnant areas tend to complicate the prediction of
dispersion coefficients because of their containment and retention of
tracer material). Yotsukura, Fisher and Sayre (4) describe more recent
efforts to calculate dispersion coefficients in a mid U.S. river system
using the methods previously described. Specific methods for predicting
dispersion characteristics in natural streams are readily available however,
it is clear that data must be gathered from each river of concern in order
to predict its individual pattern. Complete field experiments such as the
ones described in the literature need not be necessary for the Mackenzie
Valley river system. However, attention must be given each individual
river before its mixing characteristics can be determined as tracing a marker
dye in one river is of little significance in predicting the mixing character-
istics of a second.

Talks with Dr. Verschuren and associates of Civil Engineering,
University of Alberta resulted in the belief that placement of a detector for
stream sampling would become a major but not impossible task. Interesting
comments that these gentlemen offered are listed below:

i)   River currents are not necessarily the same in winter
      as in summer, the difference being caused by the
      frozen ice layer.

ii)   The addition of oil in water might not necessarily follow
      the same pattern as a dye marker due to the different
      characteristics of the fluid. Therefore they recommended
      that field tests be done with the crude oil of interest
      and under actual winter conditions.

iii) If the pipeline was built close enough to the Mackenzie
      River itself, a possible alternative location for the
      detector would be in the Mackenzie River, immediately
      downstream of the tributary and along the same bank.

iv)   Considering that much of the river data are available now,
      only the winter field tests with oil remain to be done.

v)   Distance downstream for proper detection would vary greatly
      from river to river, depending on turbulence conditions.
      In the Mackenzie drainage basin there is a wide variety
      of flow conditions. The Great Bear River, relatively not
      very turbulent, would require that the detector be placed
      at the mouth of the tributary as it empties into the
      Mackenzie. In contrast, a swift river may need only one
      meander length for sufficient mixing to occur.

The most pertinent conclusion is that field measurements from each stream
are required before an optimum detector location can be determined. Knowing
certain conditions, it appears practical by this method to establish a
prime location for the detector. As for the problem of destruction of the

detection equipment by ice or flood the only solution thus far is to bury
the system, sample the ground water and allow the channel bottom to offer
its natural protection from the elements. We might keep in mind however, that
under less demanding conditions the river water sampling technique has much
to offer.

7.2   Summary of Results for Water Sampling

Although some of the observations listed below may lead the reader
to believe there is no hope for this method, such is not the case. These
observations merely point out the complexities encountered which could be
resolved with alterations in procedures. This, however, has been given lower
priority in favour of what is thought to be a much more reliable and less
complex method: river bed sampling. Nevertheless, the observations of the
foregoing sections are summarized as follows:

1. during all testing conditions, signals were usually
   intermittent or subject to intensity changes due to
   the "wash out" effect.

2. sampling at increasing distances downstream produced
   more stable but less intense signals.

3. optimum positioning of the sampling device across stream
   will vary from river to river or model to model due to
   diverse flow patterns, but occurred at 1.25 in. from
   either edge for this model.

4. optimum results occurred when sampling near the water-
   air interface (0.25 in. below surface).

5. Atkinson Point produced a signal of less than 1/3 that
   of Prudhoe Bay.

6. individual parameters were easily analyzed but three or more

parameters were often interdependent on one another,
leading to complex problems in trying to place the
detector for maximum response.

7. because of the variations in signal response due to the
   numerous parameters involved, this system would require
   very detailed testing including field testing before the
   best workable pattern could be developed for each
   individual stream.

8. River Bed Sampling

        Once it became clear that a reasonable signal was obtainable by
sampling in this manner, it became necessary to determine the parameters on
which the intensity of the signal was dependent. The variables considered
were:

                sampler location

                oil injection rate

                sampling flow rate

                river water flow rate

                sand height above oil source

                sand type

        While these parameters were being analyzed, a new problem of
oil movement in a sand-water medium was recognized. The maximum distance
possible between sampling frits depended on movement of the oil or
its fluorescent "halo" in a horizontal as well as a vertical direction.
Resolution of this problem was attempted as related in section 9. Detailed
experimental procedure for analysis of the above parameters may be
found in Appendix B.

8.1 Results of River Bed Sampling

        The analysis in the following sections was again achieved primarily
through the use of Prudhoe Bay oil, with smaller numbers of related data
for Atkinson Point oil. Because sand tends to act as a shell in trapping
oil, the results resembled the static oil/flowing water system used in
the temperature study, with an expanded time scale due to the slower rates
of injection. The elapsed time for a signal to appear emerged as a major

positive factor in detecting oil leaks of all sizes. The rate of oil leaking into the system could be very small since the sand acted as a shell to trap the oil. Thus in time, even the smallest leak produced enough oil in the shell to result in a detectable signal.

The results in the following sub-sections are straightforward and do not require much explanation. This is an asset for this method as less complexity leads to a higher degree of reliability.

8.1.1 Sampler Location

The best sampling signal was obtained from water in the immediate proximity of the pipeline. As could have been predicted, sampling closer to the oil source provided a quicker and more intense response. Figure 18 shows that moving the sampler only 1 in. above or downstream from oil source was enough to provide noticeable changes in response.

8.1.2 Oil Injection Rate

Three oil rates were used in this test, as described in Appendix A. These three oil rates were 0.236; 0.0236; and 1.0 ml/min. Because leaking oil was now trapped in the sand, discussion in terms of oil-water ratios is no longer meaningful. Figure 19 illustrates the effect of such a variation in oil flows. As the rate of injection decreased, the time for response increased. This would lead to the conclusion that any small rate of oil is detectable, and it is just a matter of time before the detection level in the river bed sand reaches a high enough intensity.

8.1.3 Sampling Flow Rate

Tests were run with sampling flow rates of 65 ml/min up to

240 ml/min. Since the two locations used in testing this range
provided similar results (figure 18), figures 20 and 21 may be compared
directly. Therefore, it may be concluded that low to medium sampling
rates in this range show no significant difference in response other than
the increased time for the signal to appear. However, the highest sampling
rate of 240 ml/min. disturbed the intensity of response enough to make it
an undesirable condition of sampling (figure 20). Thus the optimum
sampling rate must be chosen well within an experimentally determined upper
limit.

8.1.4 River Water Flow Rate

With only 2 inches of sand bed over the oil leak there was no
"washed out" effect on the signal in changing the water flow from 0.5
to 1.5 ft^3/min. Figure 22 shows nearly identical end results for both
river water flow rates. These results may be compared with those in
section 7.1.1 to illustrate that unlike downstream sampling, river bed
monitoring is not affected by changes in water flow rates. As a matter
of interest, because of the trapped oil, the fluorescent response continued well
over 1 hour after the leak was stopped.

8.1.5 Sand Height Above Oil Source

Tests were carried out with sand bed depths of two and four
inches. Instrument results show little difference in output for the
two conditions. However, visual observations indicated the presence of a
fine oil film on the water surface at the low sand level. Tests
performed on samples drawn from the water at 1 ft. at 8 ft. distances

downstream, however, showed no fluorescent signals. Therefore, other
than the increased probability of oil permeating the surface, figure
23 shows no significant effect of changing sand bed depth.

8.1.6 Sand Type

Attempts were made to determine the best type of back fill to
use in the vicinity of the buried pipeline. Two types of river bed material
were used, one a 20-40 mesh silica sand, the other a "pea" sized gravel. The
most productive results were obtained when the immediate area above the leak
source was filled with a coarse material (pea size gravel) and the sampling
frits placed in this matrix. By using a less coarse material (20-40 mesh silica
sand) to complete the back fill, the sand acted as a barrier and facilitated a
more wide spread distribution of the fluorescent halo in the coarse matrix.
Table 5 illustrates results obtained when using three combinations of coarse
and fine back fill material and sampling only at the most distant frits ((1)
and (6)) each of which are 7 in. from the point of oil injection. In two of
three instances (types A and B) no signal was recorded from sampling
points (1) and (6). In addition oil penetrated the surface in A and B
after oil additions of 42.6 ml. and 14 ml. respectively at an injection
rate of 0.236 ml/min. The third situation, made up of a 2 in. bed of
gravel covered by 2 in. of sand was the only one to produce a signal
and retain the complete volume of 42.6 mls. of oil injected over a 3 hr.
period. In contrast results in table 6 illustrate essentially no difference
in signal between conditions A and C while the only difference in test
procedure was to sample all six frits instead of just (1) and (6). By
extrapolating the results in tables 5 and 6, one could assume that frequent

Table 5

Comparison of Three Backfill Conditions

| Time (Min.) | Turner 111 Signal (% full scale) | | | Accumulated Oil (ml.) |
	Type A. 100% Sand	Type B 100% Gravel	Type C 50% Sand 50% Gravel	
30	0	0	0	7.1
60	0	0 (Oil broke Surface)	.1	14.2
90	0	–	4	21.3
120	0	–	6	28.4
150	0	–	8	35.5
180	0	–	10	42.6

Set conditions at: water flow - 1 ft^3/min

Oil flow - 0.236 ml/min

Water level - 1.75 in.

Sampler tube - 1 in. downstream
0.5 in. above source

Sampling from - (1) and (6) only

Table 6

Comparison of Two Backfill Conditions

Time (Min.)	Turner 210 Signal (% full scale)	
	Type A 100% Sand	Type C 50% Sand / 50% Gravel
0	0	0
10	0	0
20	1	2
30	2	3
50	6	6
70	10	9
75	11	10

Set conditions at: Water flow - 1 ft^3/min

Oil flow - 0.236 ml/min

Water level - 1.75 in.

Sampler tube - 1.50 in. downstream
0.5 in. above source

Sampling from - (1) through (6)
inclusive

occurrence of sampling frits would facilitate any type of back fill material but placing the sampling frit at greater distances would require a more specific back fill combination of coarse and fine material.

8.1.7 Atkinson Point and Prudhoe Bay Comparison

River bed monitoring improves the detectability of Atkinson Point oil relative to that of Prudhoe Bay. For example, in the river bed system the Atkinson signal was more than one half that of Prudhoe oil, while in the downstream water sampling system it was only one third.

8.2 Summary of Results for River Bed Sampling

General observations made from a study of the above parameters dealing with river bed sampling are summarized as follows:

1. sand acts as a trap resulting in a build up of fluorescent signal coinciding with the build up of trapped oil.

2. under all conditions the pattern of response was uniform, with variations occurring only in intensity and time for response.

3. Since the foregoing results were a consequence of cross stream sampling which has an effect of diluting the signal, the signal intensity could be increased greatly by sampling at selected probes across the stream.

4. theoretically, any size oil spill can be detected providing enough time is allowed to build up an oil pool and therefore a signal.

5. best location for sampling device is immediately above and slightly downstream of the pipeline.

6. sampling flow rate is best kept below an experimentally determined threshold level for optimum results.

7. sand depth and water flow rate do not affect the instrument output.

8. results are easily reproduced and easily interpreted.

9. Lateral Oil Movement in Sand

If the method of river bed sampling is to be utilized it becomes necessary to determine the maximum allowable distance between consecutively placed sampling frits. Ideally, they must be practically spaced in a stream bed such that the fluorescent "halo" from the oil will be detected by one of them before the oil finds an escape route to the surface. First steps in determining these spacing distances dealt with experiments on two scales of magnitude. Local sampling was used in the river model to determine which sampling frits were carrying the signal, and to what level of intensity the signal was being produced. In addition, tests on a larger scale were initiated using a 45 gallon barrel with carefully chosen sampling positions and a sand depth equal to twice the diameter. Detailed analytical methods are given in Appendix C.

9.1 Results of Lateral Movement Tests

The results indicated a surprisingly wide spread of oil around the point of introduction without any penetration to the sand surface. Results of tests performed in the river model were the most encouraging due partially to the high degree of suction at the sampling frit attracting the surrounding water soluble fluorescent compounds. However tests performed on a larger scale (in a 45 gallon drum) with reduced interference from the suction effect showed similar results of lateral movement with respect to vertical penetration of the sand by the oil, indicating the withdrawl of sampling water is not a major factor in producing fluorescence signals at lateral distances from the point of leak.

9.1.1 Test in River Model

Since the oil was injected through the center port, frits (3) and (4) were closest to the source at 1.5 inches, while (1) and (6) were the farthest away, at 7.2 inches. Frits (2) and (5) were positioned at a medium distance of 4.2 inches. Figure 24 illustrates the effect of sampling in the immediate vincinity of the leak. With only 8.3 ml. of oil present the signal more than doubled to 32 units with only valves (3) and (4) open. With only this much oil, however, the contribution from (1) (2) (5) or (6) was zero, showing that the spread of oil was limited in the lateral direction. The dilution effect of cross stream sampling with all 6 valves open is illustrated as well. Figure 25 indicates to what extent the signal was detectable at the outer edges of the model. Region I indicated a signal of 25 units from sampling at (1) and (6). As stated in Appendix C, 50 ml. of oil was injected into the system over a 3 hour period. Since each location tended to eventually exhibit an intense fluorescence signal, the results implied that the soluble fluorescent material was drawn toward the frits from which the sampling water was withdrawn. Even more encouraging results were obtained when no trace of the 50 ml. of oil was visible on the water surface. Thus, lateral movement was detected at a distance of twice the depth of sand covering the oil source before any oil penetrated the surface. The pattern of a porous "pea" gravel as a base and a more dense sand above acting as a barrier seems to provide excellent results.

Instead of relying completely on the natural ability of the oil to spread laterally through the sand, a compromise method involved sampling the six frits across the stream in a sequential manner for five minute durations each. With this approach, the continuous

monitoring of ground water would not include any dilution effect in the signal due to complete cross-stream sampling. Figure 26 illustrates the typical kind of response to be expected when sampling sequentially across the stream. Compared to the signal response the base line is still relatively stable. It could be deduced from this chart that the point of oil injection was bordered by frits (2) and (3) since signals from these locations are the only ones systematically increasing, thus there is an added advantage of being able to locate the source of the oil leak.

9.1.2   Mid Scale Static Test

Since two gallons of oil were required for this test and supplies of oil were limited, the injection was made up of nearly equal quantities of three oils: Prudhoe Bay, Atkinson Point and a sweet oil from I.P.L. This test brought two questions into focus: where and how quickly does the fluorescent "halo" appear and where and how quickly does the oil appear. Appendix C, section 5 gives a legend to probe locations. Following is a list of events describing the movement patterns of the fluorescent "halo" and the oil, for conditions described in Appendix C:

1. Fluorescence signal and the oil first appeared at (5, 2 N) after the addition of 1800 ml. of oil.

2. Continued additions of oil totalling 4500 ml. produced a detectible signal at (0, 11) as well as a signal of less intensity but still equally detectible at (10, 2 N).

3. After 6500 ml. of oil was added oil finally became visible at (0, 11), but by this time the fluorescence signal at

(10, 2 N) was strong and easily detectible.

4. Continued addition of oil to 7400 ml. merely increased the fluorescence signal at (10, 2 N) but no oil was drawn from this point. This total injection took place intermittently over a three day period but oil still had not appeared at the sand surface.

From these four observations it may be summarized that the fluorescent "halo" was detected at a horizontal distance of 11 in. from the source before the oil actually appeared at a vertical distance of 11 in. from the source. This result occurred with a total sand cover of 22 in.

9.2 Summary of Results for Lateral Oil Movement

Observations made in the foregoing sections may be summarized as follows:

1. The fluorescent "halo" is partially drawn to the sampling frit due to the suction applied.

2. Tests in the river model gave a fluorescence signal at a lateral distance from the source twice as great as the depth of sand cover.

3. Sequential sampling in the river bed has the advantage of providing intense signals combined with optimum distances between intake frits.

4. Tests in the 45 gallon barrel showed a fluorescence signal at a lateral distance of 11 in. from the source while the depth of sand cover was 22 in.

10. Recommendations

The work reported above shows that the principles of fluorescence detection for pipeline leaks are well founded. In particular it appears possible to detect small oil leaks in pipeline stream crossings most easily by methods of river bed sampling. However, all results were obtained from scale models and work should next commence on pilot projects ultimately leading to a complete workable field unit.

Recommendation: that investigations into the fluorescence detection unit be extended as outlined in the following detailed recommendations:

(a) Sampling Methods

(i) River bed sampling clearly yields fluorescence signals of greater intensity and stability than those from stream sampling. In addition, further benefits accrue in the river bed pattern from the fact that the sampling unit is protected in the river bed from natural hazards such as ice scour. Nevertheless, stream monitoring is still valuable, particularly for systems in which monitoring is required for seepages of oil that may enter streams from leaks at points along the pipeline other than at river crossings.

Recommendation: that further development of leak detection by fluorescent means be undertaken, primarily for the river-bed system, but also for the water-stream system.

(ii) In the current work water in the simulated river bed was sampled through a glass frit. Obviously this kind of device is not directly applicable to a river bed. Further, a number of other aspects dealing with flushing, piping, valving and sequencing require careful development in order to assure the integrity and credibility of the

sample.

Recommendation: that design work be carried out

for appropriate river bed sampling devices leading

to a workable field model.

(iii) The laboratory simulations reported above took place on a
very small scale. It is not possible to project them quantitatively
into a field situation. In particular, the point dealing with length
and spacing of sampling units requires extensive definition.

Recommendation: that pilot projects be undertaken to

define the size and spacing of sampling units through the

mounting of field experiments.

(iv) Although the river-bed approach seems clearly preferable
over the stream-sampling method for pipelines leaking at river crossings,
the latter method still has much merit, and it may be used in special
situations in which oil enters the stream from sources other than the
pipeline below the stream.

Recommendation: that a limited volume of work be under-

taken to improve the stream monitoring method.

(b) Analytical instrumentation

(i) The demands to be placed on field instrumentation in terms of
sensitivity, reliability and durability are very severe. The instrument
must be simple, rugged, redundant and to some degree self correcting.
Provision must also be made for ready accessibility and simple
maintenance. This requires a special design that must be developed with
these principles in mind; it will not be sufficient to try to modify
existing equipment.

Recommendation: that a suitable field instrument be
designed and constructed, firstly at a bread
board level, secondly at a prototype level.

(ii) The fluorescence signals obtained in the current work
using standard laboratory units were limited in intensity.

Recommendation: that special design work in electronics be
carried out to give enhanced signals through electronic
suppression of background noise that is peculiar to
the system.

(iii) Fluorescence signals operated at the site of the river
crossing must be transmitted in some manner to a central monitoring
unit.

Recommendation: that a program be established to determine
the interface specifications between the leak detection
unit at the river-crossing and an overall telemetry system.

(c) Cost/benefit design factor

The indicated principle for detection of pipeline leaks may
assume a number of different physical expressions ranging for example
from a simple system in which samples of water are taken weekly and
monitored monthly by an operator, to a sophisticated system in which
real time sampling is carried out with internal checks every few minutes,
with fluorescent scanning to reveal spectral quality and with redundant
circuitry and back-up electronics to give extremely reliable continuous
data. Obviously the cost of such detection system will increase sharply
with advancing sophistication. An evaluation should be made of the

benefits to be achieved as a function of the cost of providing the
system.   This cost-benefit analysis would call for the consideration
of a number of amenity factors in addition to many direct operational
factors such as costs of cleaning up oil spills of various sizes.

Recommendation: that provision be made for a cost/benefit
analysis on pipeline leak detection as a guide to the
degree of sophistication required in the proposed fluorescent
method of detection.

(d) Priorities

Priorities for carrying out the foregoing studies may be
established in terms of (a) overall importance, and (b) temporal urgency.
Sequencing in a time-framework seems to be the most suitable approach at this
time. It is recommended that the work be sequenced as follows:

1. that a pilot project as described in parts two and three
of sampling methods be undertaken in conjunction with
electronic amplification and damping of signals as
described in section (b ii).

2. that a rugged instrument be designed and demonstrated
as called for in section (b i).

3. that specifications for telemetry of monitored signals
be established and cost benefit studies be undertaken.

4. that further work on stream sampling be given a low
priority in terms of overall importance, but provision
be made so that this could be begun at any point in
the developmental work should it appear desirable to
do so.

(e) Operational Aspects

The work proposed as a result of the present study is more comprehensive than that reported here. It calls for a variety of approaches ranging in complexity from laboratory design and simulation to the conduct of field tests. It seems logical to co-ordinate such studies in a single overall approach so that the various segments of the topic can be developed together. Further, it seems reasonable that the people responsible for the early work would be the best fitted for the conduct of the next phase of development.

Recommendations:

1. that a prime contractor be assigned for the completion of the development of the detection system.

2. that the prime contractor be the University of Calgary through its Environmental Sciences Centre (Kananaskis).

3. that the prime contractor assign the various elements of the development program, in consultation with the funding agency, to its own laboratories or sub contractors, according to the availability of qualified personnel and appropriate facilities.

APPENDIX A

METHODS OF DOWNSTREAM SAMPLING IN WATER

Data produced in section 7. were based on the following sequential procedure:

1. By regulating two inlet valves, the water flow rate of the model was established at three levels: 0.5 ft^3/min, 1.0 ft^3/min and 1.5 ft^3/min.

2. The depth of water was standardized at 2.25 in. by adjusting the baffle heights, one at the inlet and one at the outlet reservoir. Thus, the water movement was through a level trough 16 ft. long. The flow reflected the run-off or overflow over the outlet baffle.

3. The sampling water was drawn off via a vacuum trap through a 1/4 in. O.D. stainless steel tube, reducing to 1/8 in. O.D. and channelled through a Turner model 111 fluorometer. With the help of a section of flex stainless steel hose, this sampling tube could be placed in any location across the width of the stream.

4. The optical system of the Turner 111 instrumentation was improved with the addition of an "off the shelf" reflecting ultraviolet filter capable of blocking out all but light below 300 nm with peak transmission of 26% occurring at 253.5 nm and a band width at 13% transmission of 13.6 nm. (See 3. Instrument Design

for figure 1 and further details). Coupled with the
Turner 111 fluorometer was a Hewlett Packard recorder
model 7127A and range module model 17501A. Because
of the low signal to noise ratio, the capacity of this
recorder allowed amplification of the Turner 111 signal
output by decreasing the full-scale millivolt setting.

5. Signals were recorded relative to a stable background
   level, achieved by allowing 30 min or more for the
   entire apparatus to reach an equilibrium.

6. Introduction of the oil was through a series of septums
   mounted across the underside width of the trough, by
   means of a model 355 Sage syringe pump. The rates of
   oil selected were 0.236 and 0.0236 ml/min. The
   oil-water flow ratios thus provided were:
   0.0236 ml/1 ft^3 or 1/1.2 million; 0.236 ml/1 ft^3 or 1/120,000
   0.236/1.5 ft^3 or 1/180,000;   0.236/0.5 ft^3 or 1/60,000

7. Chosen arbitrarily were downstream sampling distances of
   1 ft. and 8 ft. Also arbitrarily were the sampling
   heights below the water surface, chosen at .25 in, .50 in,
   .75 in. and 1.75 in.

8. The cross-stream location of the sampler was in one of
   three places, which may be interpreted through the
   following diagram:

The two locations labelled (1) and (6) were symmetric about the centre location (C).
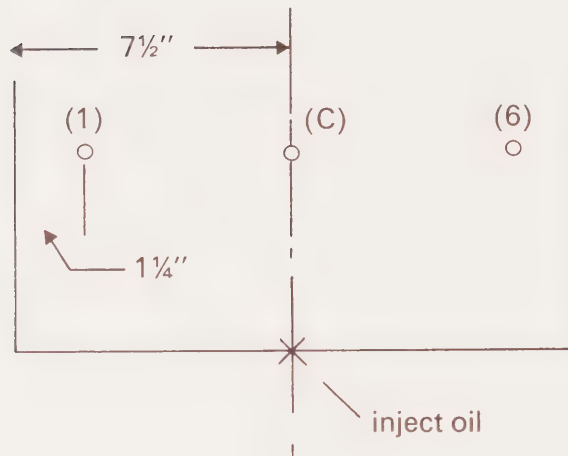
9. The variables listed in section 7. could not be treated independently and their individual effects interpreted through comparison of selected graphs and other related data.

APPENDIX B

METHODS OF RIVER BED SAMPLING

Data produced in section 8. were based on the following procedures:

1. Water flow rates were regulated according to procedures in Appendix A. In addition, the first section of the river model (4.5 ft. long) was filled to a depth of 4 in. with a 20-40 mesh silica sand. The remainder of the river model was left clean primarily to avoid the use of a large volume of sand.

2. The baffle holding the sand in place also allowed a water level of 1 3/4 in. to develop above the sand.
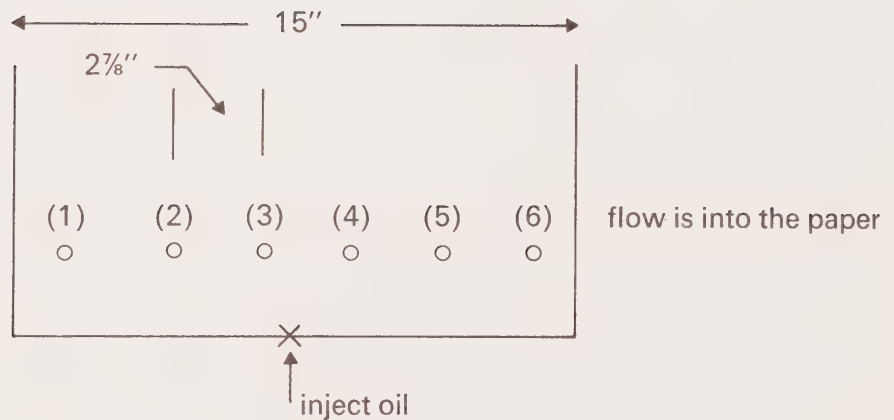
3. The configuration of the sampling apparatus is shown in photograph 4. The six sampling frits were spaced at an equal distance of 2 7/8 in. staggered between the injection ports, and each with an individual shut-off valve. This design facilitated sampling total stream width or portions of it, the purpose of the glass frits being to keep unwanted foreign particles from passing through the flow cell. A legend for locating each of the valves by symbols is located on page 49.

4. The Turner 210 spectrofluorometer was the main instrument used in this segment of testing. Upon comparison of the two instruments (the Turner 210 and Turner 111 with recorder) it was found that under standard settings the sensitivity of the two instruments was almost identical, thus allowing direct comparison of results from both instruments.

5. Signals were recorded relative to a stable background level, achieved by allowing up to 2 hours of sampling flow before the oil leak was started. It was a time necessary to reach a steady transmission of light.

6. For most experiments the oil flow was 0.236 ml/min. Together with a water flow rate of $1 \, ft^3/min$, this provided an oil/water ratio of 1/120,000. All parameters considered were analyzed with this oil-water combination. In addition, oil leak rates of 0.0236 and

1.0 ml/min. were used to break down the effect of oil
injection rates. The ratio of 1/1,200,000 or 0.0236 ml/min.
oil to 1 ft^3/min water was chosen on the basis that it
represented (by extrapolation) an oil spill of 10 bbl/hr.
into a stream of 20,000 cfs. These were realistic figures
arrived at after it became known that an oil spill of
10 times this magnitude in a 48 in. O.D. pipe would be
difficult to detect by material balance without intensive
monitoring, and even then it would take at least 1 or
2 days for detection.

7. Placement of the sampling tube varied, but only
    by small increments. The graphs and results are
    discussed in terms of the sampler being a distance above
    (↑) and distance downstream (←) from the point source
    of oil injection.

8. Only two sand depths were used (4 in. and 2 in.) to
    reveal the effects of the degree of sand cover. In
    studying sand type, 20-40 mesh uniform silica sand
    was used as well as sand with a base of "pea" gravel.
    The pea gravel bed formed a solid rectangle across the
    stream measuring 3 in. on each side of the sampler and 2 in.
    in depth. Surrounding the gravel on 3 sides was the
    silica sand to a depth of 4 in. in total. This provided just
    enough gravel to cover the sampling frits and allowed the
    dense sand to act as a barrier, thus preventing the oil
    from penetrating the surface.

9. Unless stated otherwise all results were based on oil
   injection at the centre and sampling through all 6 frits.
   To avoid having oil run through the system, the "leak"
   was usually stopped after a volume of 8.3 ml was injected
   or after 35 min. at the standard rate of 0.236 ml/min. Thus
   the tail end of the charts is shaped accordingly. The
   free hand reproduction of each chart has attempted to
   give the reader a feel for the size of signal to noise
   ratio resulting from the choice of instrument settings
   used. With the compressed time scale used, the actual
   signal to noise should appear as a solid line 1 or 2 units
   in thickness.

APPENDIX C

ANALYTICAL METHODS FOR LATERAL OIL

MOVEMENT IN SAND

A brief history of experimental methods for section 9. is outlined below:

A. The following statements apply to selected cross-stream sampling using the scale river model:

    1. Sand bed in both tests discussed totalled 4 in.

    2. The bed type used in the test producing figure 25 had a gravel core around the sampler as described in Appendix B, section 8. The type of bed used in the test producing figure 24 was a uniform 20-40 mesh silica sand.

    3. Results in figure 24 were obtained with a sampler placement of 1/2 in. above the oil source and an accumulated oil reservoir of 8.3 ml. analysed 30 min. after shut-off of a 0.236 ml/min. oil rate.

    4. Results of figure 25 were for a sampler placement 1 1/2 in. downstream and 1/2 in. above the source as well as an accumulated oil reservoir of 50 ml. analyzed 20 min. after shut-off of two consecutive oil rates of 0.236 ml/min for 156 min. and 1.0 ml/min for 10 min.

B. The following statements apply to selected sampling in the 45 gallon drum:

    1. The sand type was a 30-40 mesh silica sand.

    2. Seven hundred pounds of sand and 20 gallons of water brought

the sand level to 22 in. above the oil source, a
distance equal to the diameter of the barrel, and
left a 4 in. cap of water covering the sand.

3. A 1/8 in. O.D. copper tubing was inserted 4 in. into the
    bottom center of the barrel. Using this as the oil
    injection point allowed a sand base of 4 in. to soak
    up the oil thus keeping the oil from contacting any portion
    of the barrel when first injected. Completing the
    oil injection line was a 1 liter stainless steel vessel
    pressurized with nitrogen with a control valve after the
    vessel to regulate the oil flow to approximately 1.25 liters/hr.
    Thus, 1 liter charges of oil were introduced into the
    system over 45 min. intervals. The time between charges
    was considered unimportant and varied between 2 hrs. and
    16 hours.

4. A total of six probes of 1/8 in. O.D. copper tubing, covered
    at one end with a layer of cloth to keep out the fine sand
    particles, were placed at locations of high interest.

5. The probes were all placed along one diameter and their
    location referred to by stating their radius distance in
    inches and their height in inches measured relative to the
    point source of oil injection. Probes on opposite sides
    of centre were referred to as North (N) or South (S).
    The notation to follow is radius (r), height (h) and
    (N or S) or (r, h, N) or (r, h, S).
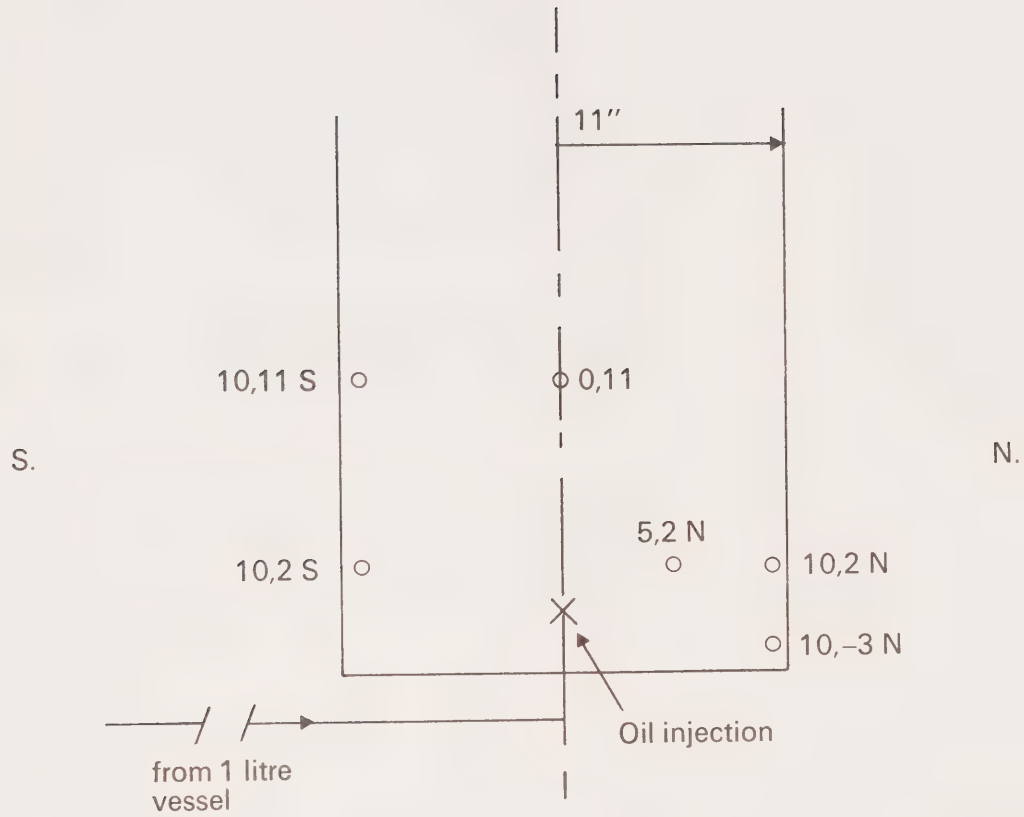
6. The probes were sampled by applying suction and
drawing off small quantities of water and monitoring
them statically in the Turner model 111.

APPENDIX D

References

(1) Hodgson, G.W., M. Strosher, E. Peake, M.T. Strosher, 1972, A Feasibility
          Study on a Proposed Method for the Detection of Oil Leaks
          Into Water. Unpublished ALUR Report, Department of Indian
          Affairs and Northern Development, Ottawa, 31p + xxix.

(2) Fisher, H.B., 1967B, The Mechanics of Dispersion in Natural Streams:
          Jour. Hydraulics Div., Am. Soc. Civil Engineers, V. 93, No.
          HY6, p. 187-216.

(3) Fisher, H.B., 1968, Methods for Predicting Dispersion Coefficients in
          Natural Streams, with Applications to Lower Reaches of the
          Green and Duwamish Rivers Washington. United States Geological
          Survey, Professional Paper 582-A.

(4) Nobuhiro Yotsukura, H.B. Fisher, W.W. Sayre, 1970, Measurements of Mixing
          Characteristics of the Missouri River Between Sioux City, Iowa,
          and Plattsmouth, Nebraska. United States Geological Survey
          Water Supply Paper 1899-G.
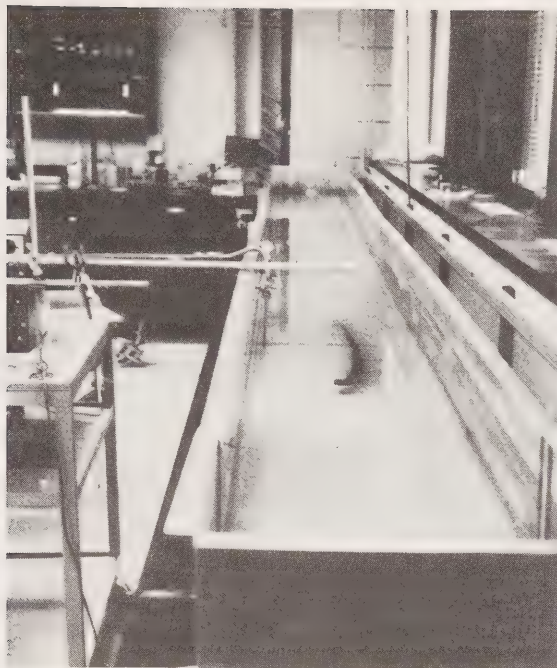
Photograph 1
River model without the sand river bed. Inlet reservoir is in foreground.
Notice the 2 ft. plume of oil built up from a 0.236 ml/min. oil injection
rate and a (slow) water flow of 0.5 ft^3/min. This particular configura-
tion yielded a poor signal since the sampler was located 1.25 in. from
the edge of the trough.
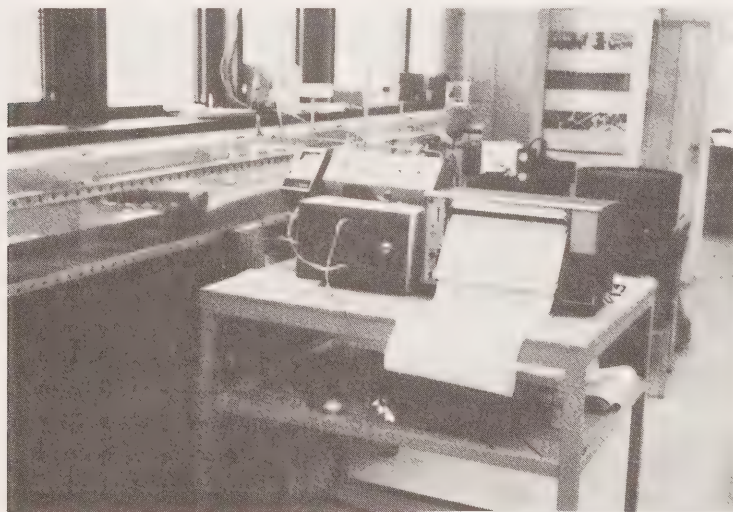
Photograph 2
Photograph showing overall view of testing operations. Fluorometer
(Turner 111) and recorder are located on a moveable stand with the river
model in the background.
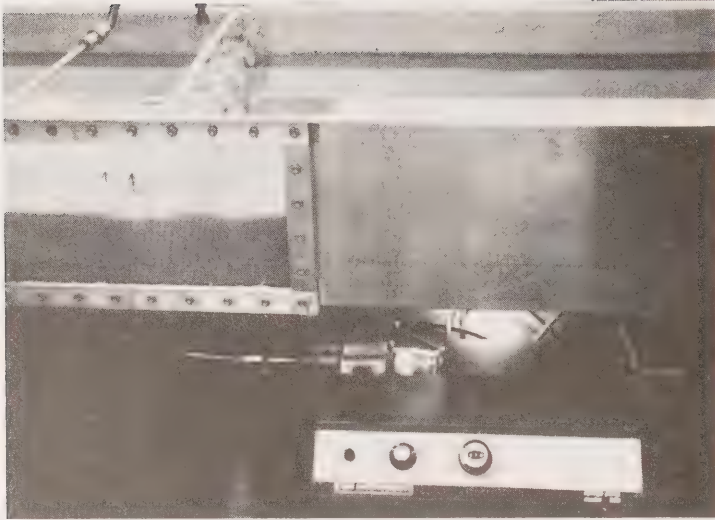
Photograph 3
Close-up of sand sampling and oil injection area. The oil is injected
beneath the sand and water in the sand sampled through 6 samplers across
the stream, all leading to a common line supplying the flow cell. Water
flow is from right to left.

Photograph 4
Photograph showing close-up of glass apparatus for sampling water in the
sand bed. According to the legend for locating the sampling valves
(Appendix B section 3) valves (3) and (4) in this photograph are closed.
Height from cross bar to tip of glass frit is 5 in. while length in total
is 14.5 in.
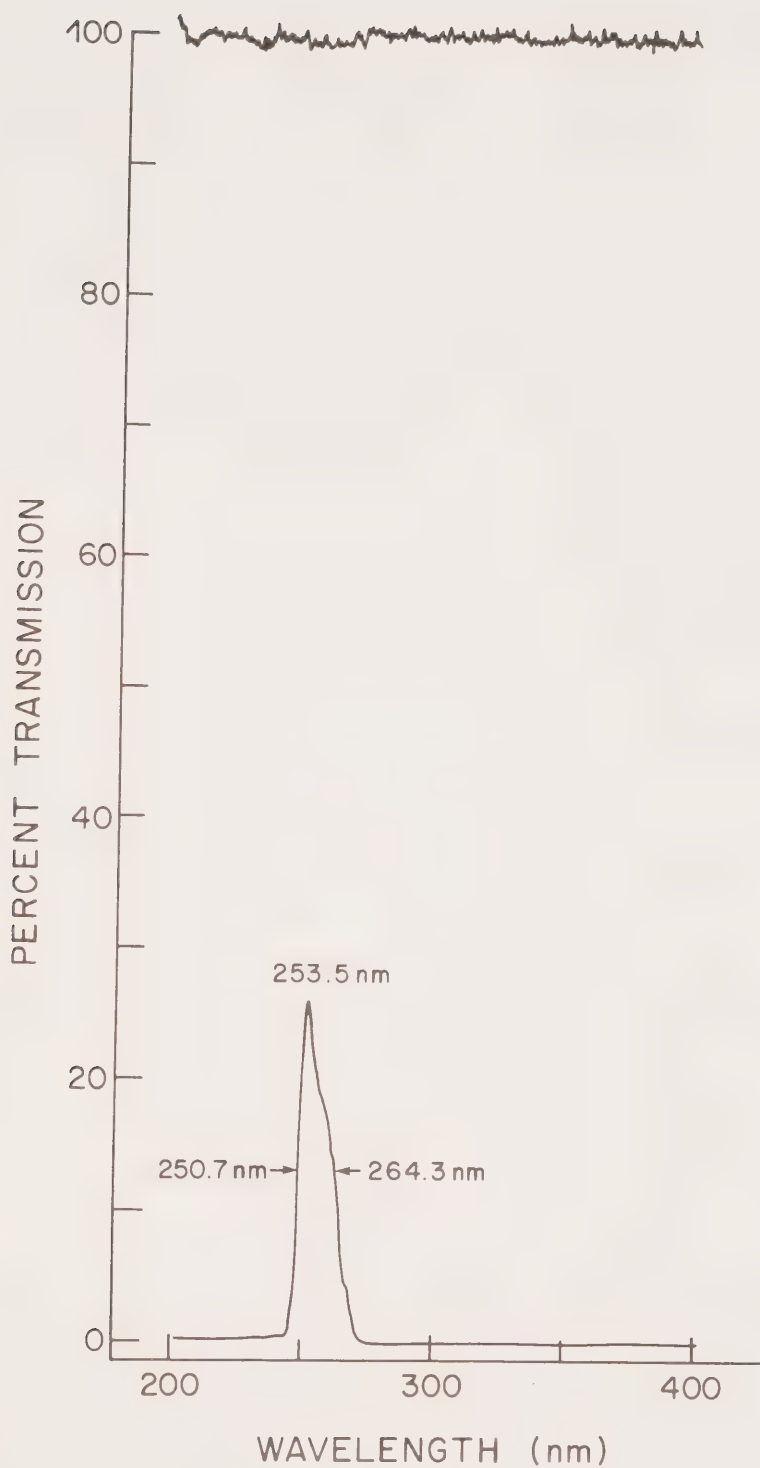
Figure 1

Percent transmission curve illustrating performance
of reflecting ultra-violet filter for the Turner
model 111. Note that essentially no light is
transmitted beyond 300 nm.
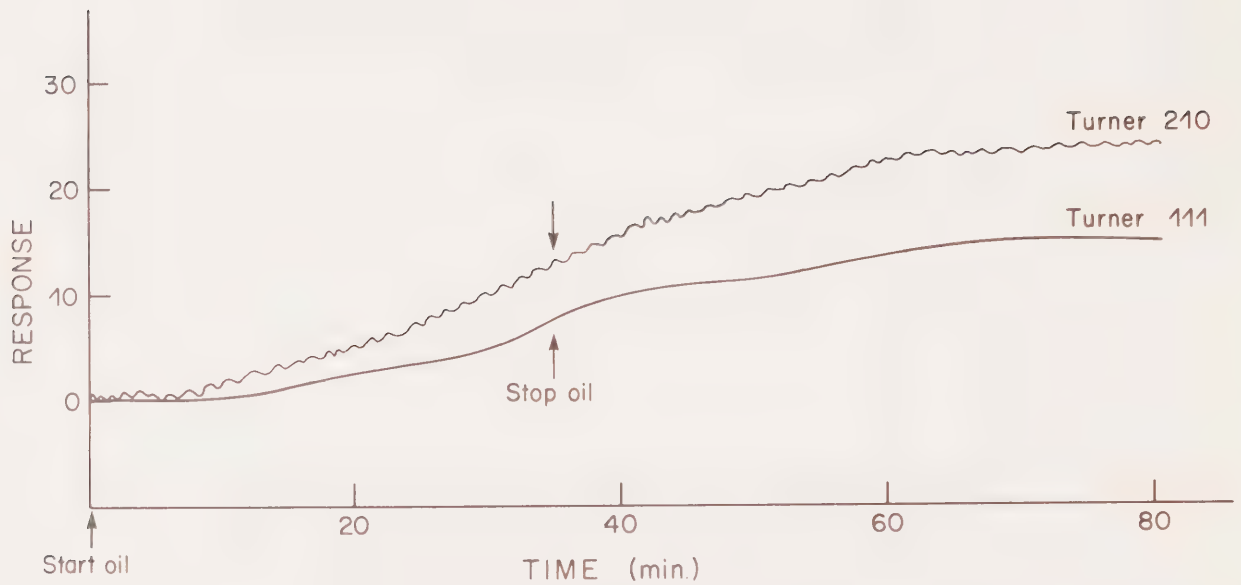
Figure 2

Comparison of the two instruments (Turner 210 and
111) illustrating the difference in signal from
the same test. Later, the Turner 111 results
improved, with the addition of a more versatile
recorder.
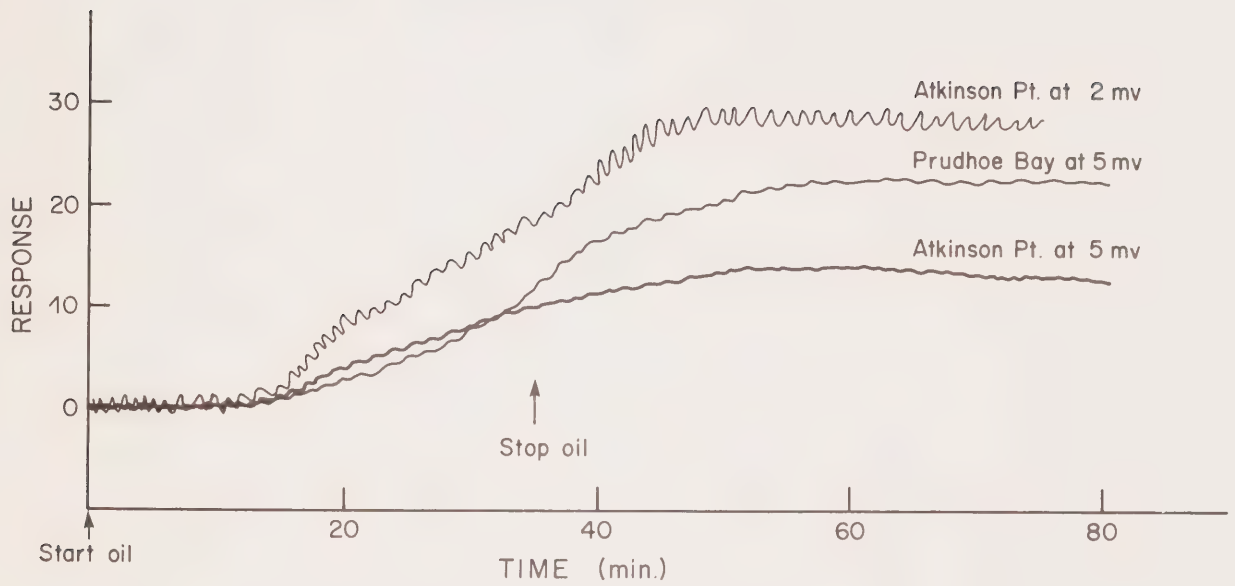
Figure 3

Sand bed sampling with both Atkinson Point and
Prudhoe Bay oils. This test shows a comparison
of tests involving Prudhoe Bay and Atkinson Point
oils using the Turner model 111 at a 5 mv setting,
as well as a comparison of variations in mv
settings and the corresponding change in intensity
and signal to noise ratio.
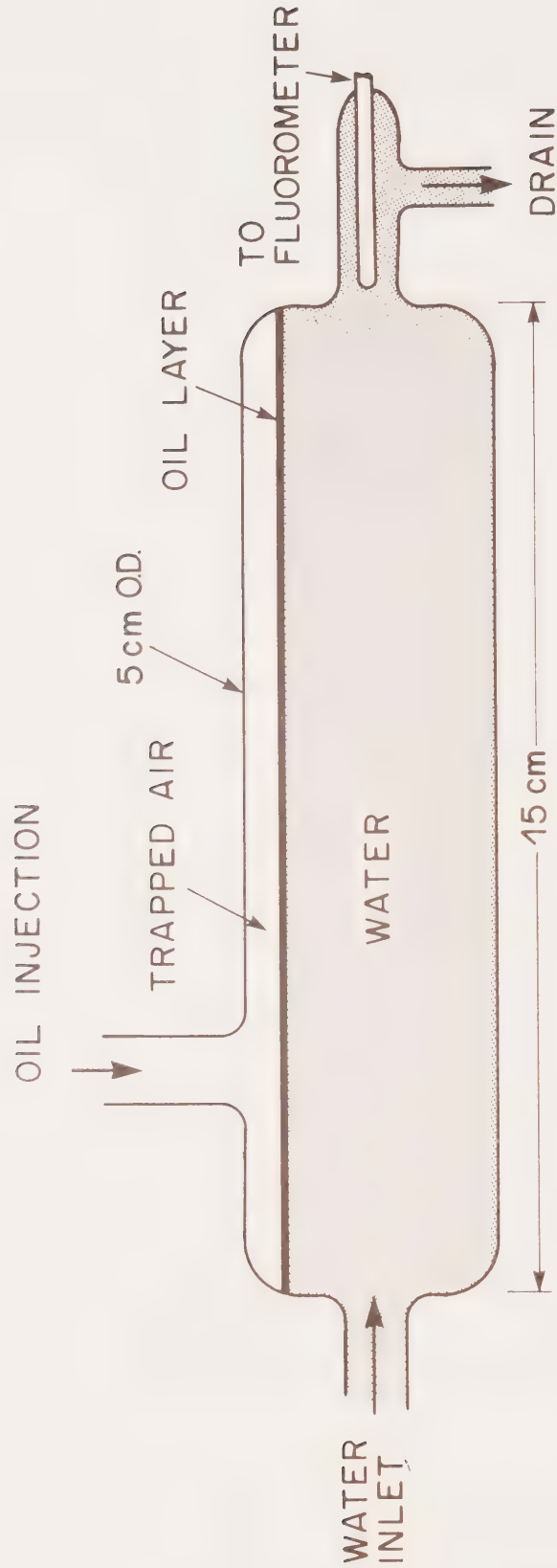
Figure 4
Flow cell used in cold temperature study for contacting
oil with flowing water.
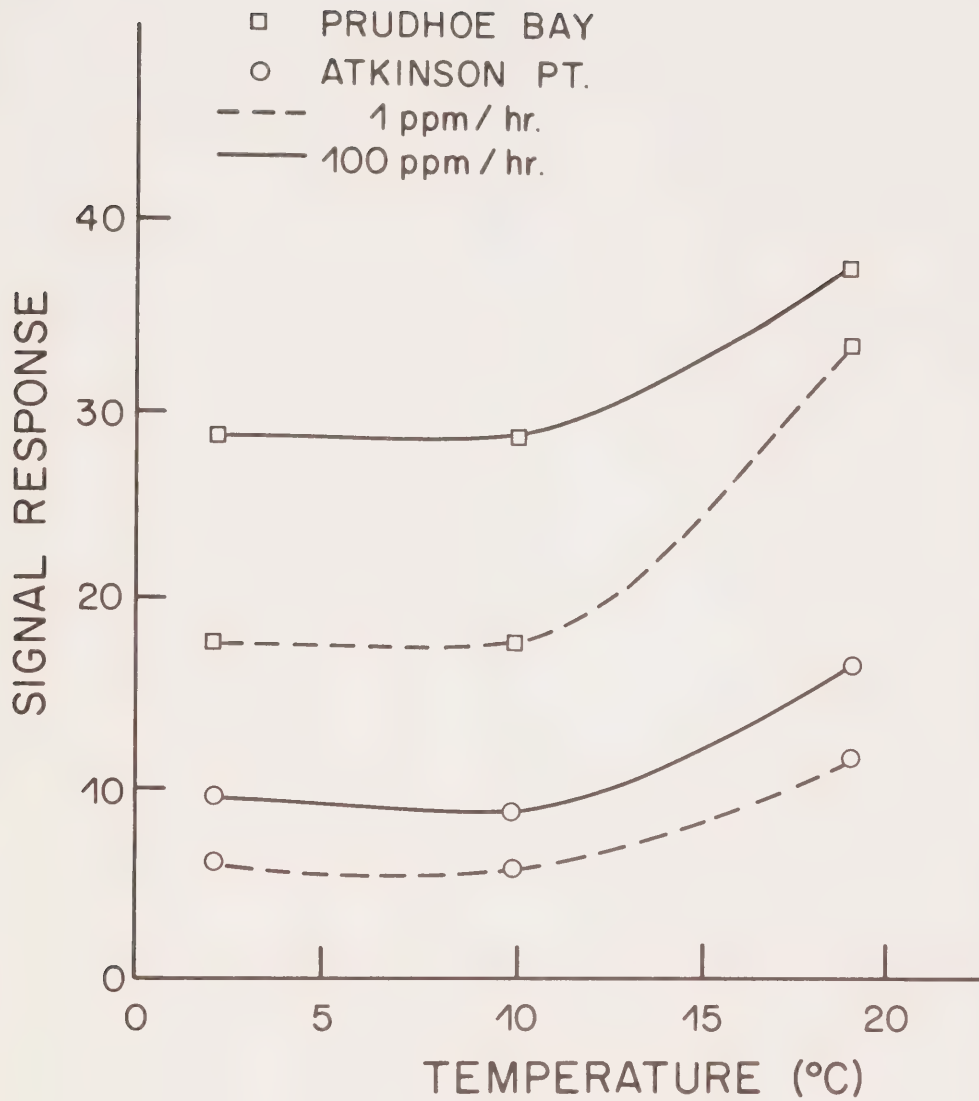
Figure 5
Comparison of response for Prudhoe Bay and Atkinson Point oils at three
temperatures and two oil concentrations.
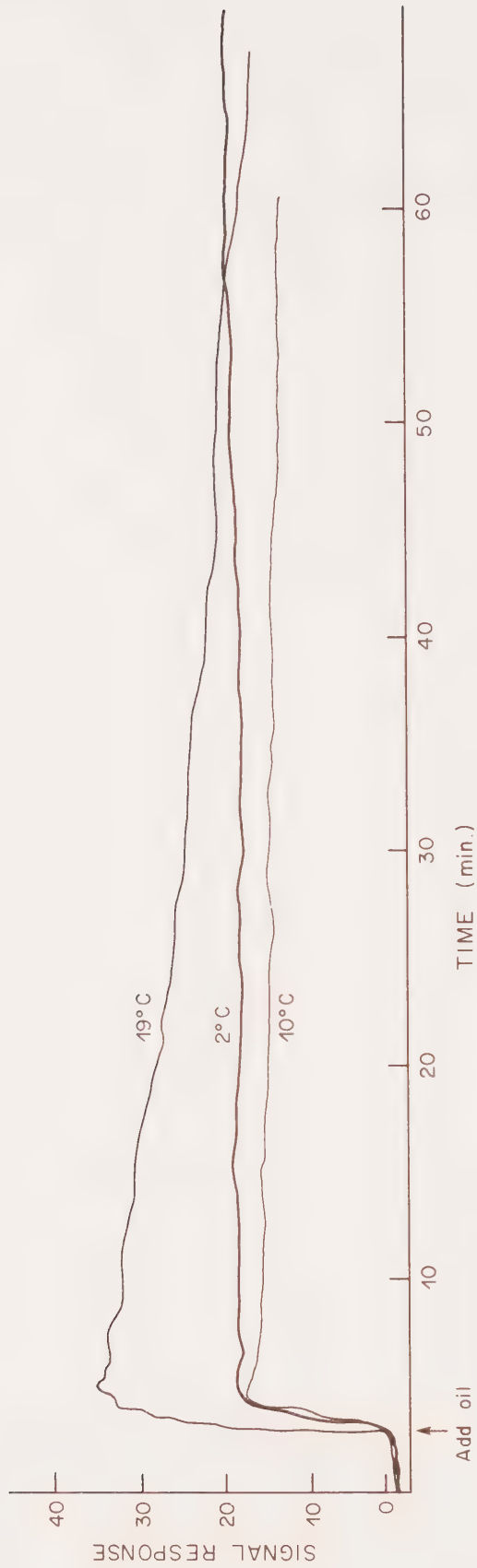
Figure 6

Fluorescence response for Prudhoe Bay oil at
three temperatures tested over a 60 min. time
period.
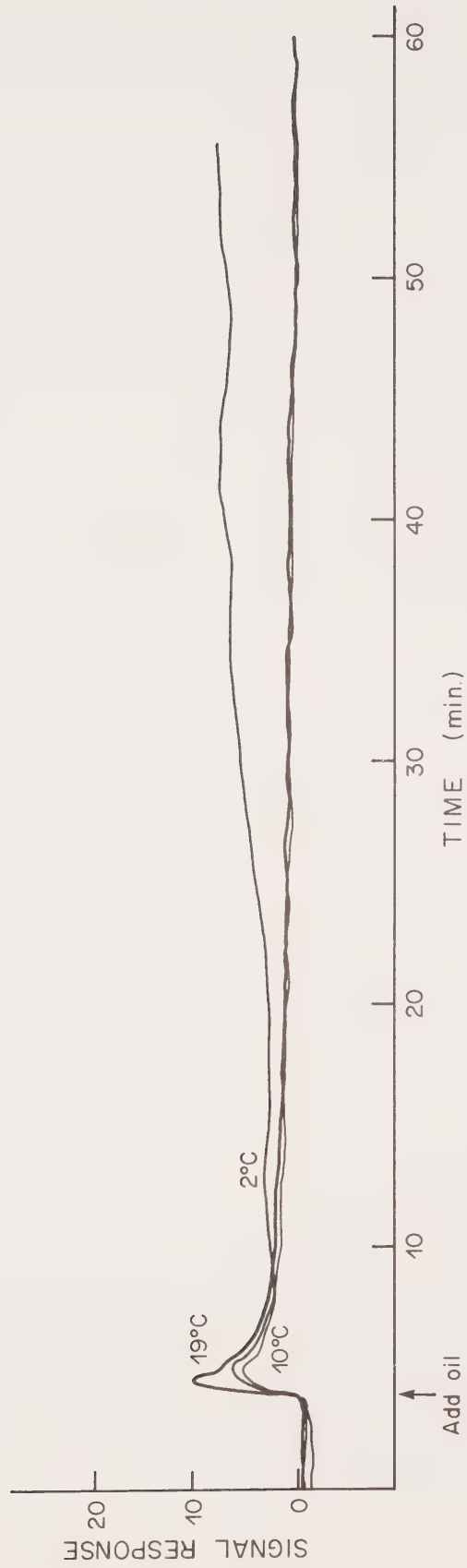
Figure 7

Fluorescence response for Atkinson Point oil at three temperatures tested over a 60 min. time period.
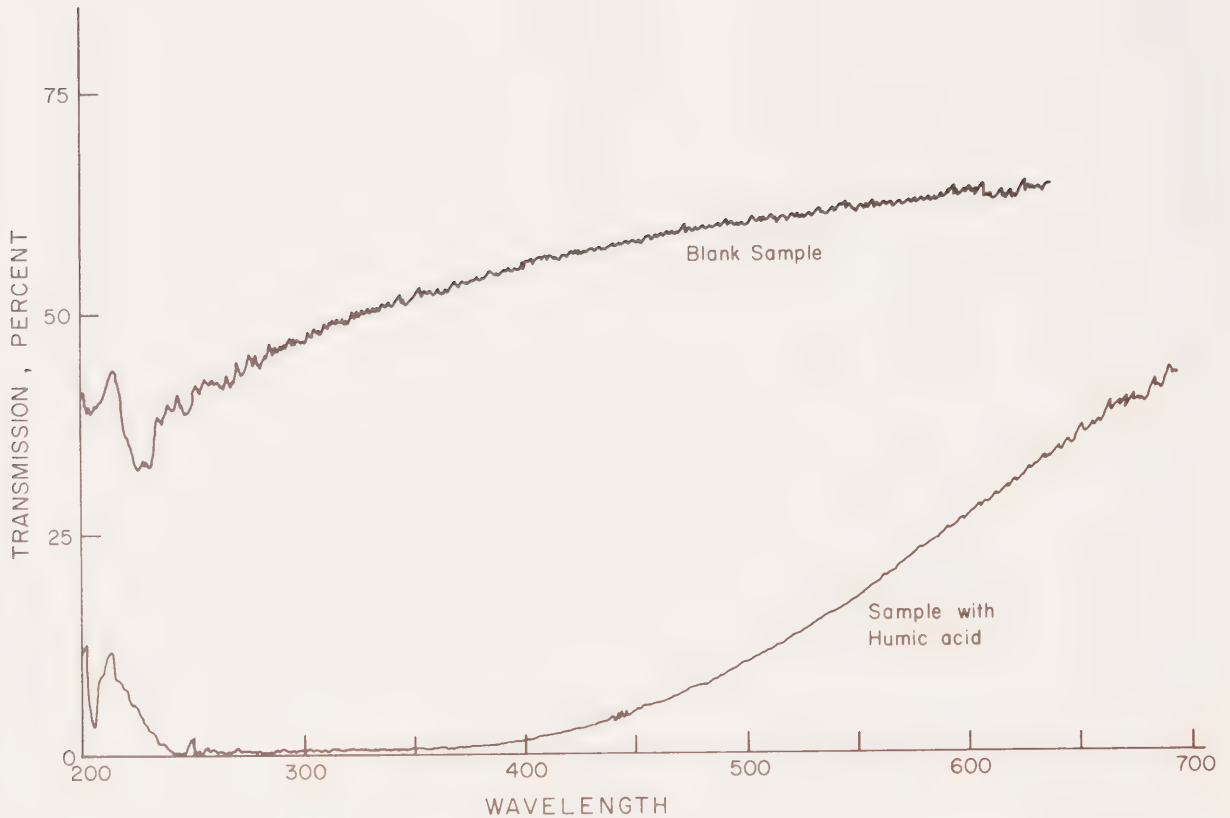
Figure 8

Per cent transmission scan of river water sample
#d4460 as a blank and after the addition of a
dissolved colored material in the water (humic
acid). Note the zero level of transmission at
the wavelengths of interest (250 to 400 nm).
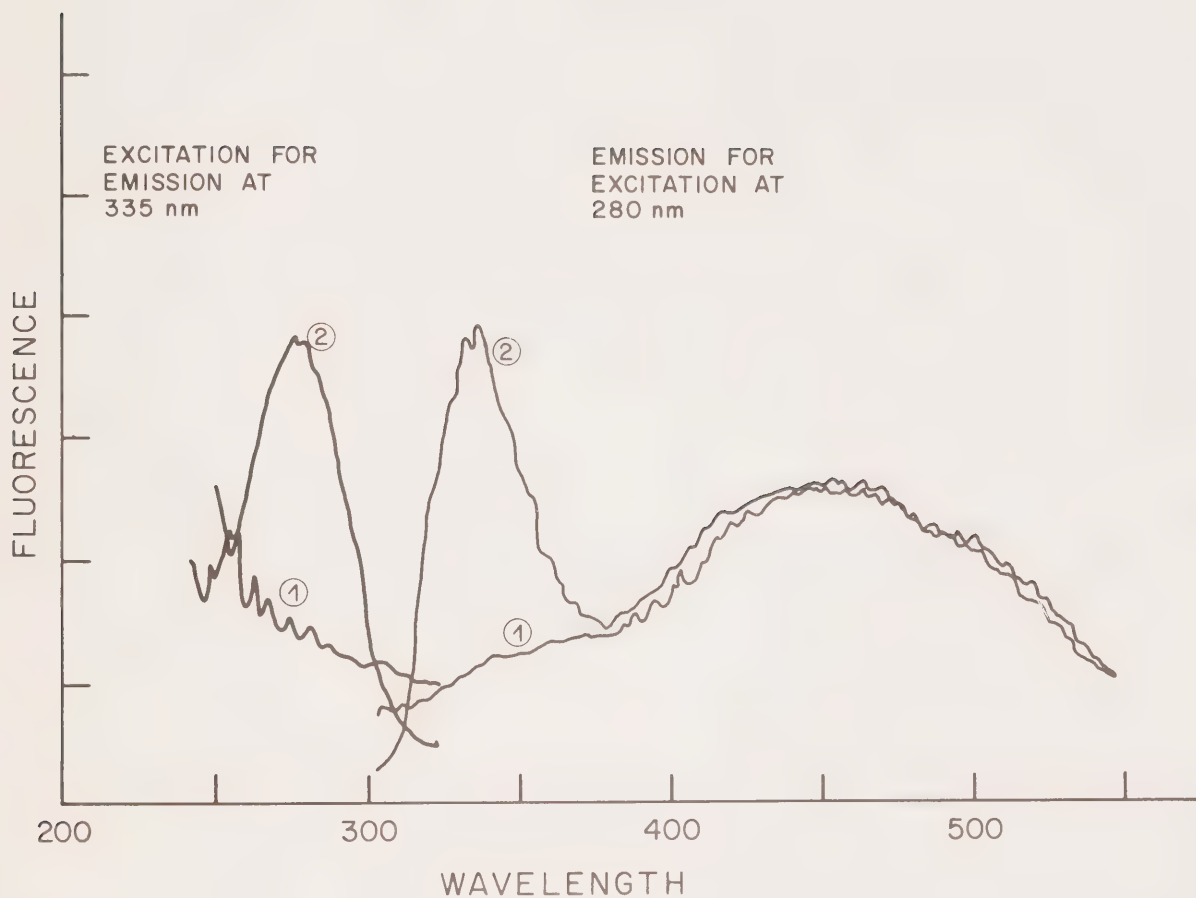
Figure 9

Fluorescence scan of river water sample #d3373
with normal sediment load (1) showing little
interference at fluorescence maxima (280/335 nm),
and scan of same sample after adding 1 ul/ml
fluorescent material (methyl naphthalene) showing
good fluorescence response (2).
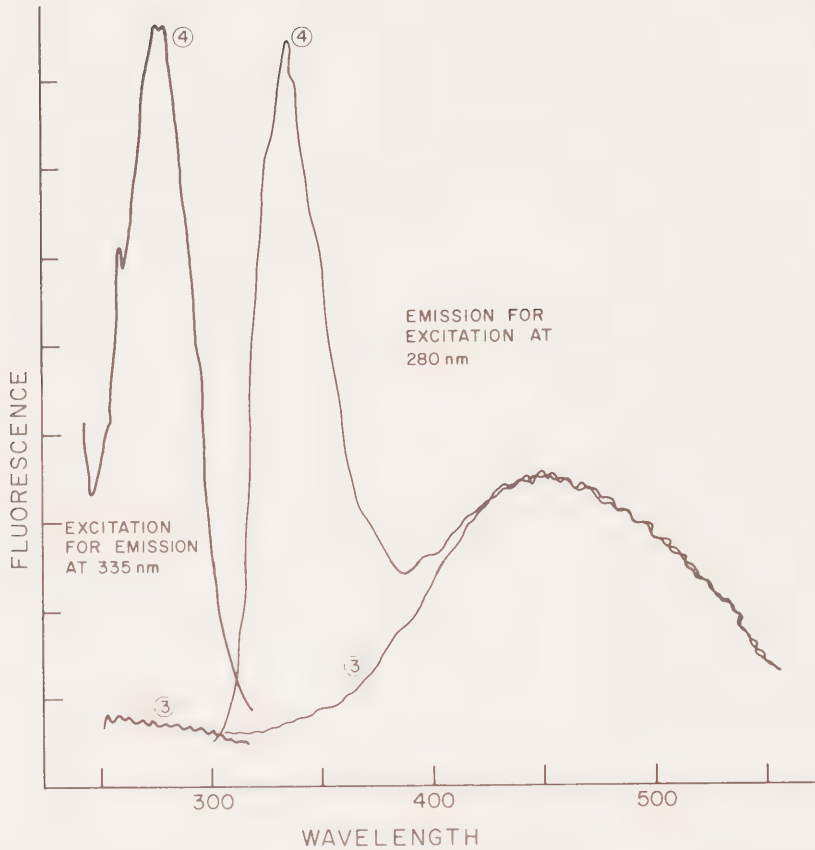
Figure 10

Fluorescence scan of river water sample #d3373
after settling for 24 hr. (3) showing no inter-
ference at fluorescence maxima (280/335 nm) and
scan of same sample after adding 1 ul/ml fluorescent
material (methyl naphthalene) and settling for 24 hr.
(4) showing strong fluorescence response at 280/335 nm.
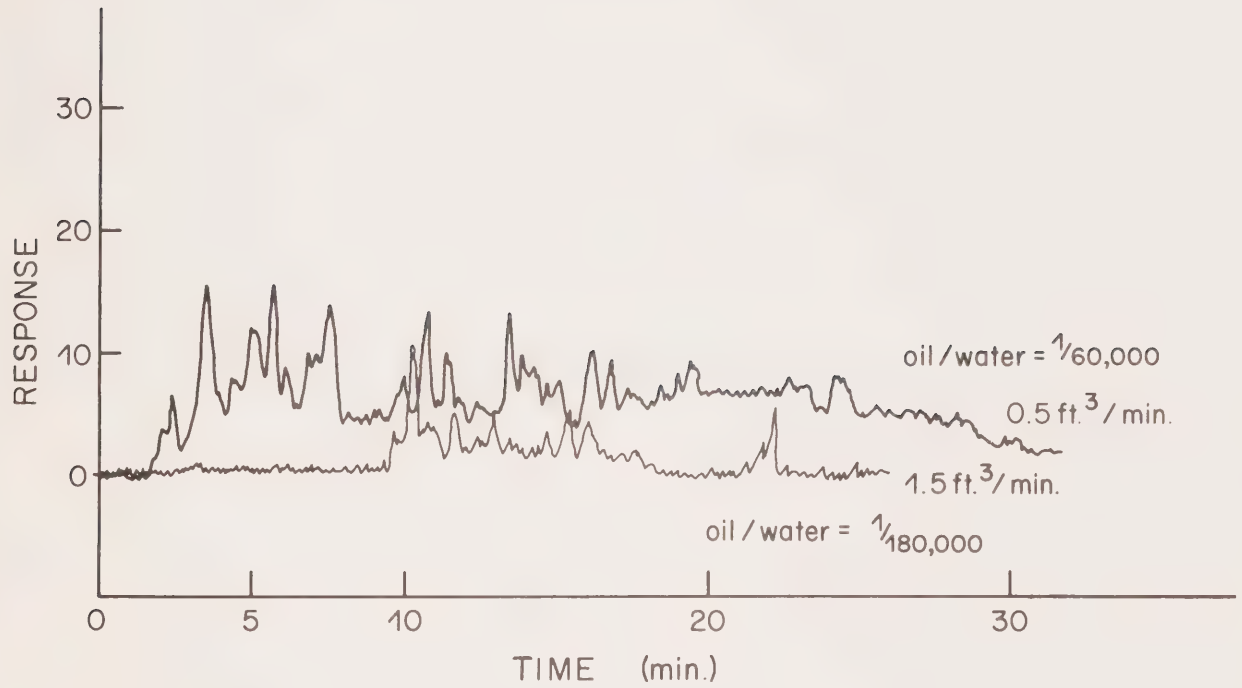
Figure 11

Fluorescence response illustrating the effect of
changing the oil/water ratio by varying the water
flow. Sampling took place 1 ft. downstream from
the leak.
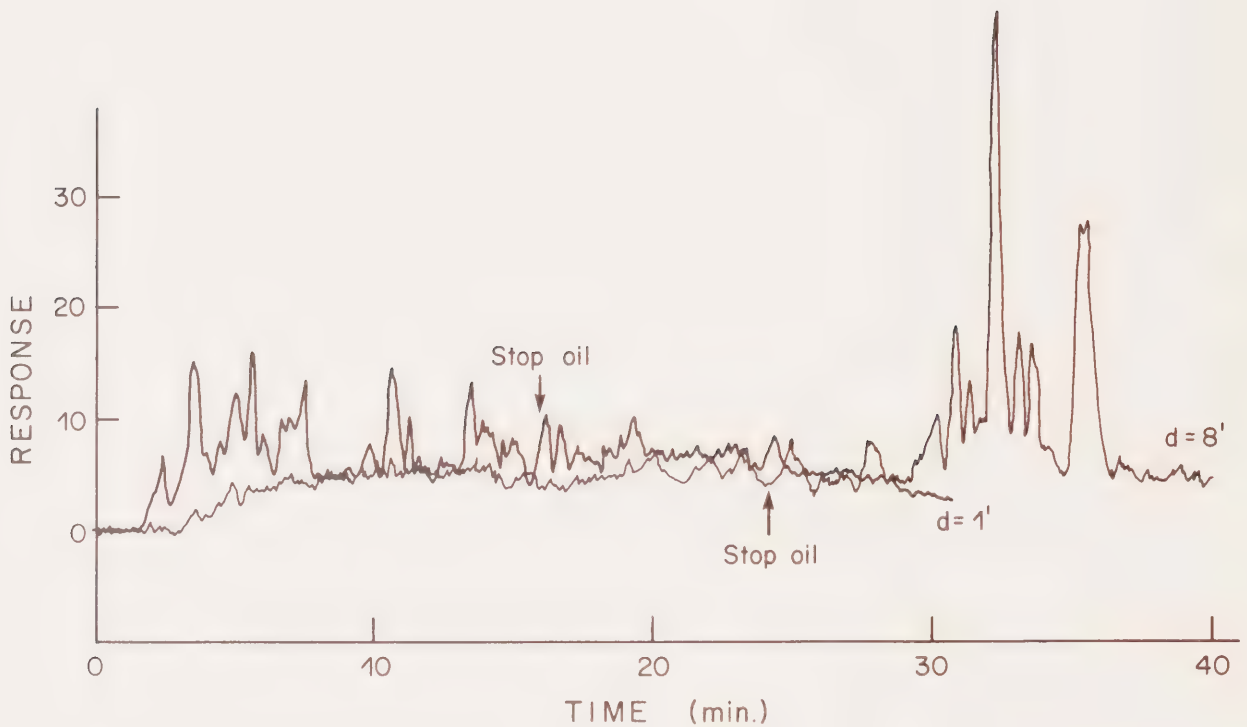
Figure 12

Fluorescence signal illustrating the effect of
changing the downstream distance "d" from source
to sampler. Distances of 1 ft. and 8 ft. were
chosen arbitrarily with all other parameters held
constant.
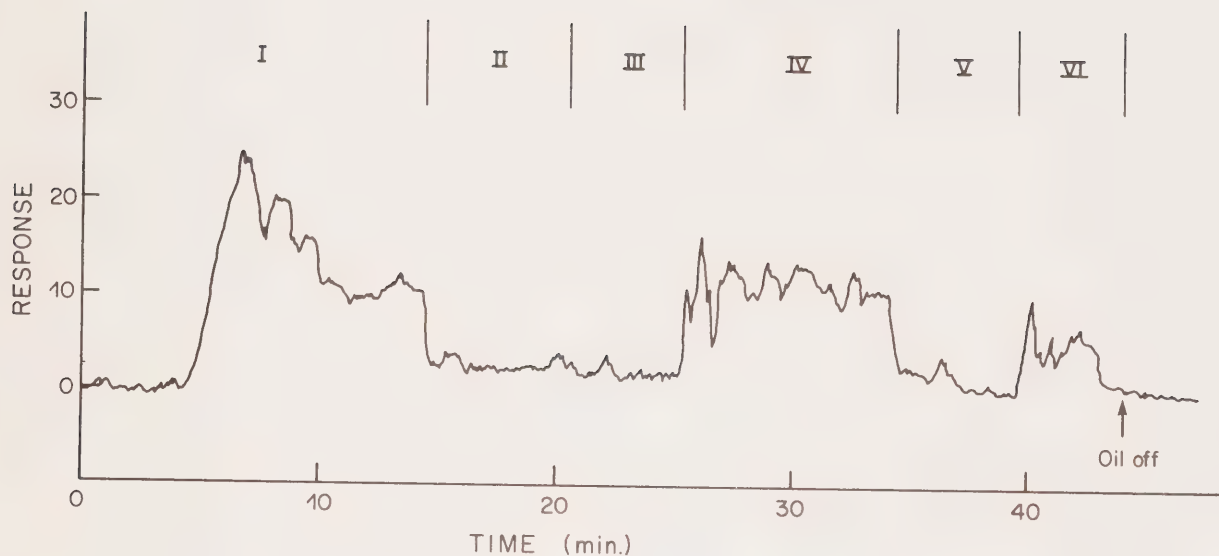
Figure 13

Fluorescence response of a continuous test
involving variations in flow and location as
listed below. Refer to Appendix A section 8
for legend to cross stream locations. The
following symbols are defined for easy reference:

    L: location of sampling device across stream
    h: depth below water surface of sampler
    Q: Water flow rate of river model

With a constant downstream distance of 8 ft. and
an oil injection rate of 0.236 ml/min the conditions
of each region were as follows:

I	h = .25"	Q = 0.5 ft^3/min	L = (1)
II	h = 1.75"	Q = 0.5 ft^3/min	L = (1)
III	h = .25"	Q = 0.5 ft^3/min	L = (C)
IV	h = .25"	Q = 0.5 ft^3/min	L = (6)
V	h = .25"	Q = 1.5 ft^3/min	L = (6)
VI	same condition as V but mechanical mixing taking place 2 ft. upstream of sampler location.		
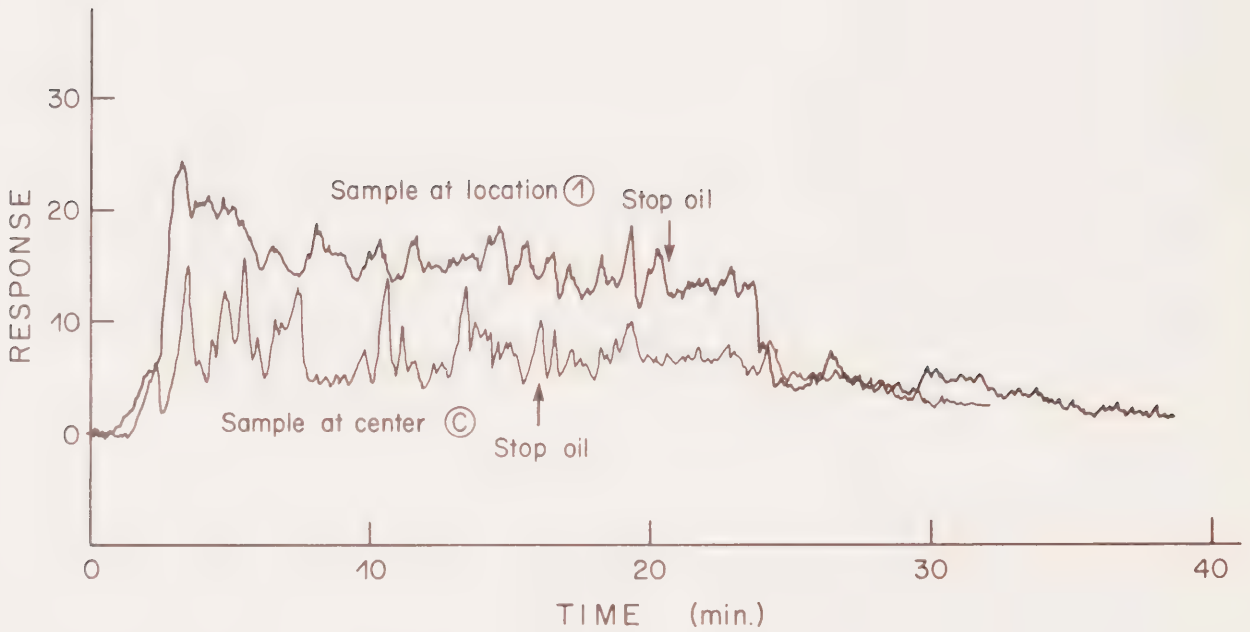
Figure 14

Fluorescence response showing effect of sampling
at various points across the stream. Refer to
Appendix A section 8 for legend to cross stream
locations.
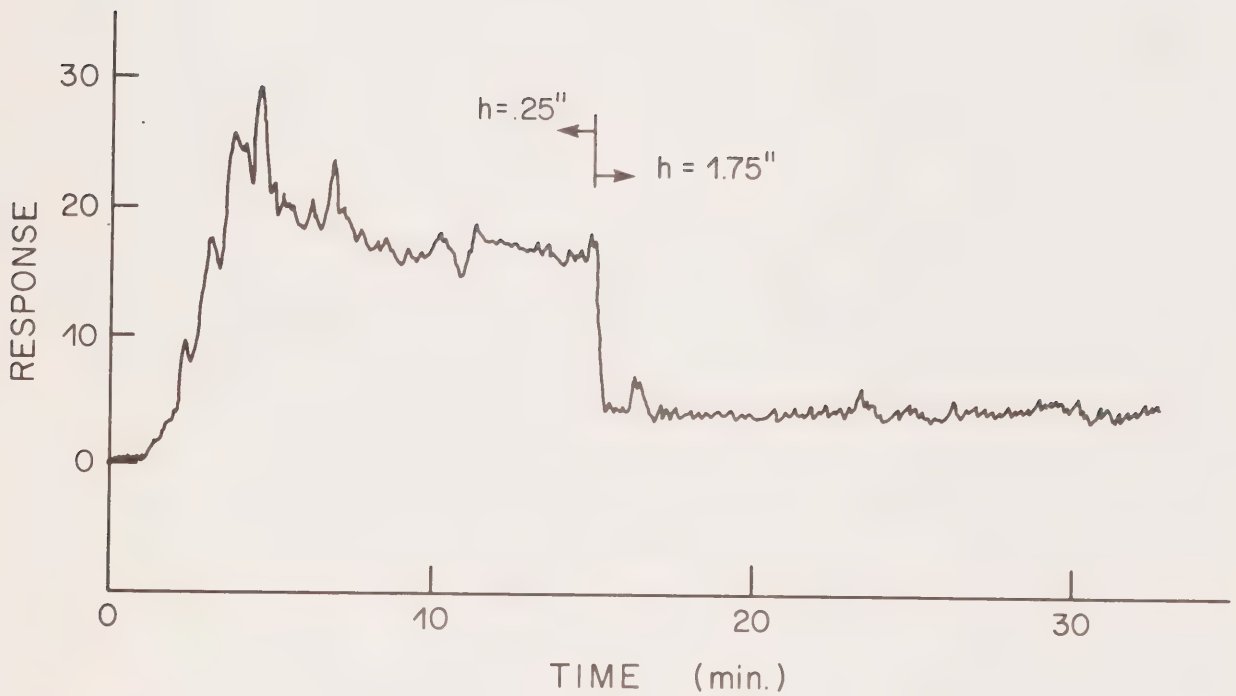
Figure 15

Fluorescence response for sampling at two depths
below the water surface, .25 in. and 1.75 in. The
test was continuous with the change in depth of
sampling device taking place at 15 min. coincident
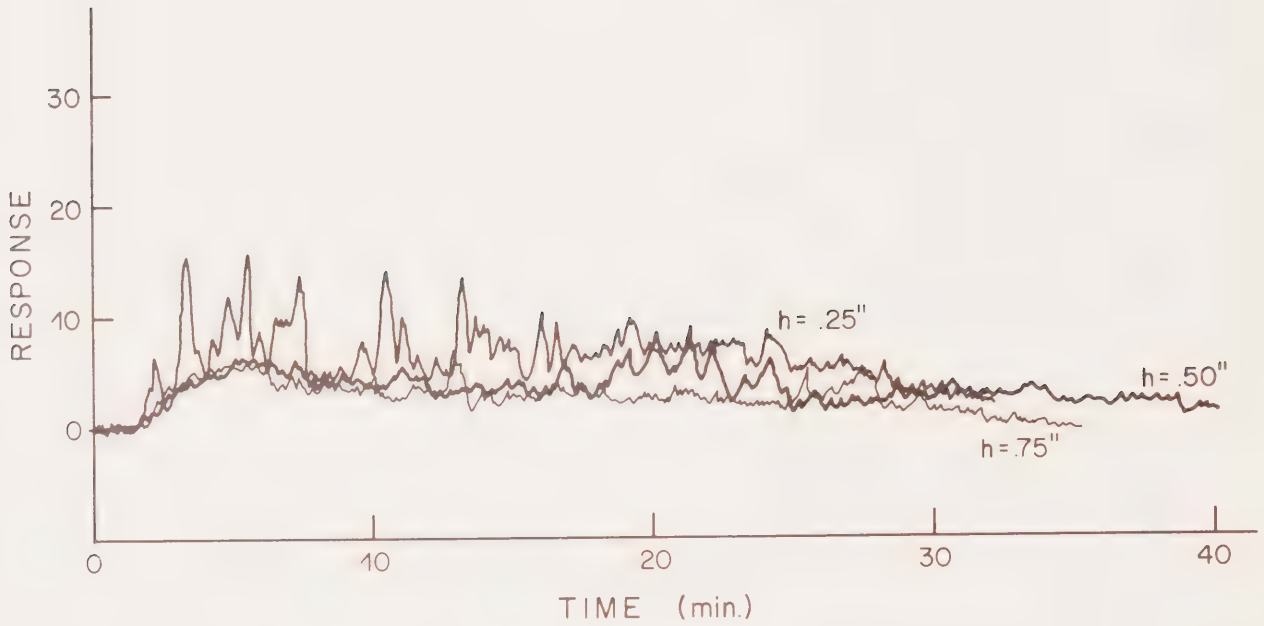with the sharp loss of signal.

Figure 16

Effect of sampling at various depths below the
surface of the water. Fluorescence response de-
creased gradually with these small increment in-
creases in depth.
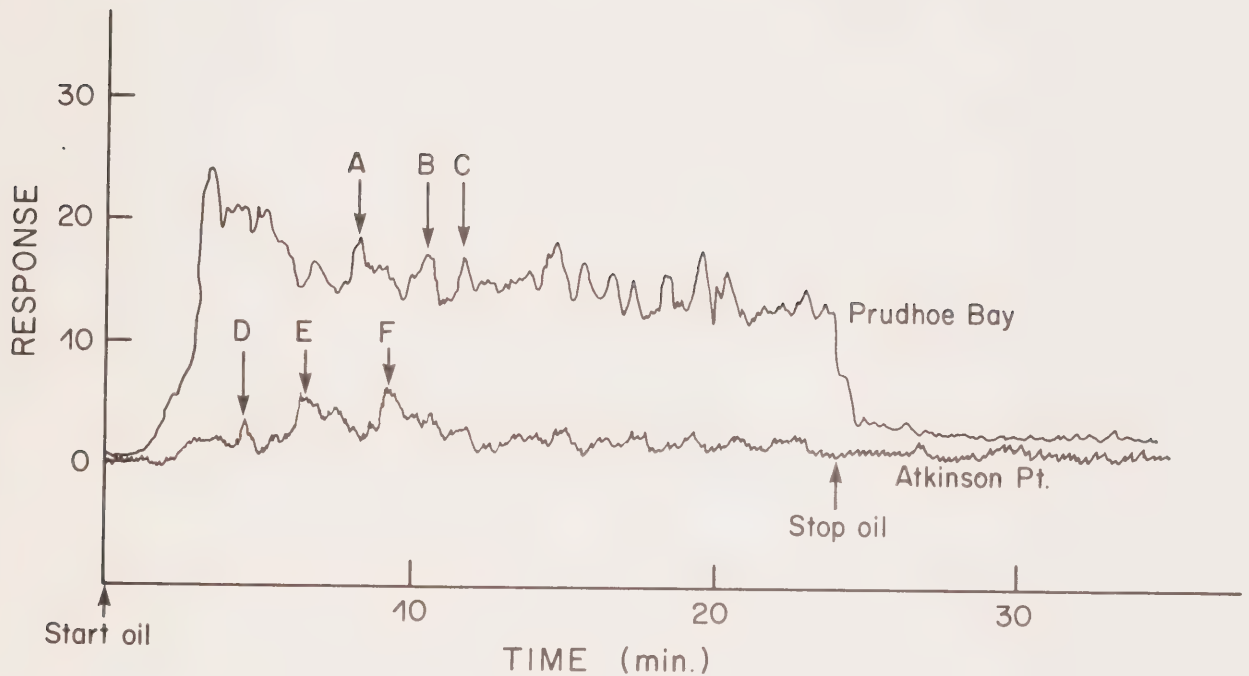
Figure 17

Response in downstream water sampling comparing
Atkinson Point and Prudhoe Bay oils. In each case,
the conditions were an oil/water ratio of 1/60,000;
downstream distance of 1 ft; a cross stream location
of 1.25 in. from edge; and a depth below surface of
0.25 in. The signals peaking at A, B, C, D, E and F
were all due to concentrated fluorescent pools caused
by intermittent droplets of oil bursting at the water
surface. These therefore were real responses, not to
be attributed to instrumental noise.
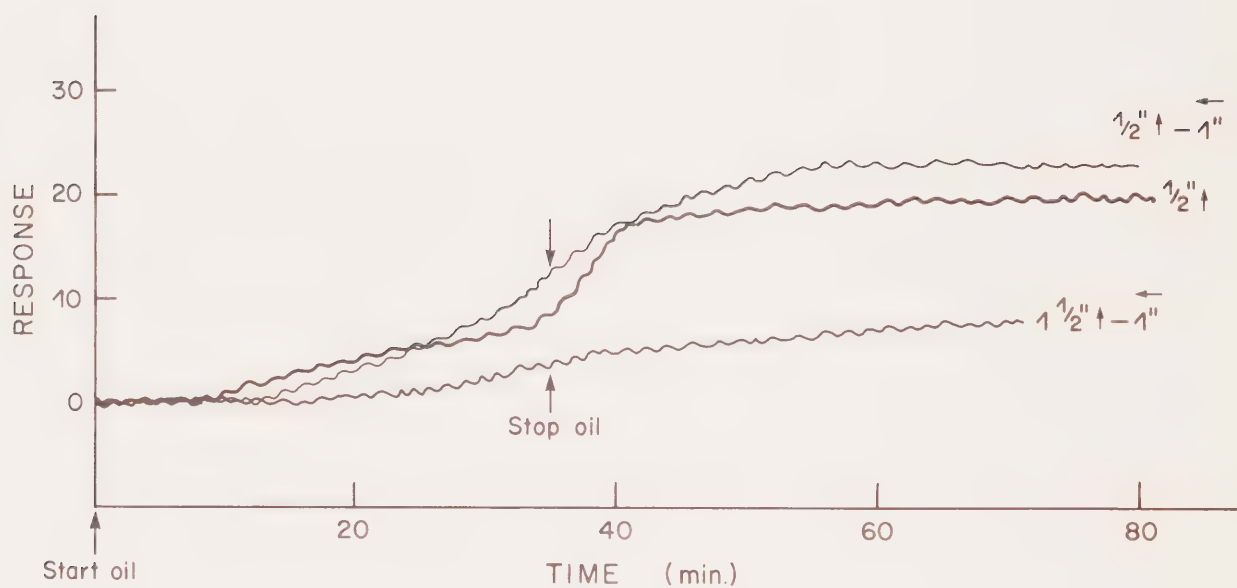
Figure 18

Effect of sampler location in river-bed sampling
using Prudhoe Bay oil. Note the low intensity of
signal for the test located furthest from the oil
source. Notations (←) and (↑) indicate distances
downstream and above oil source respectively.
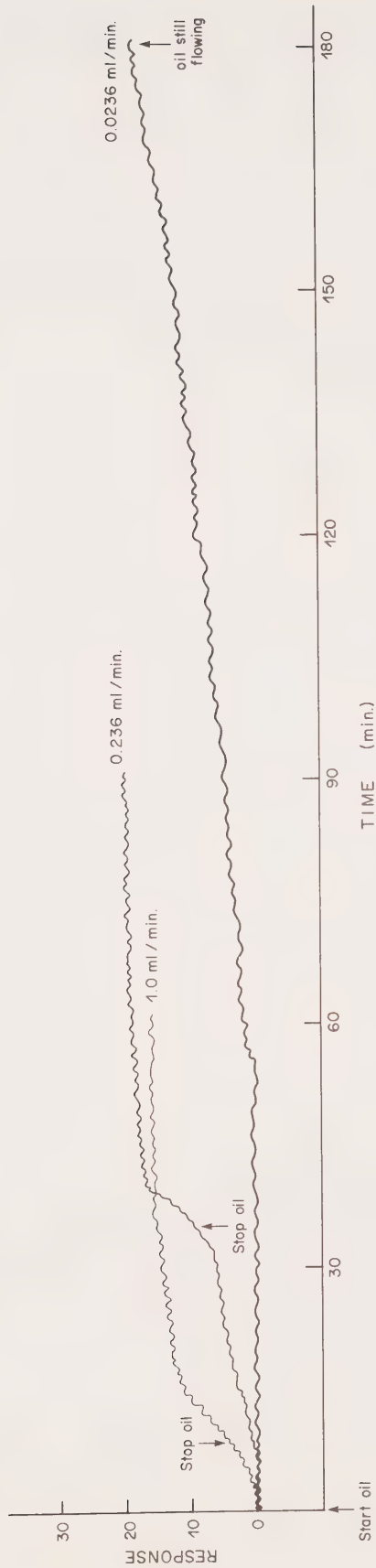
Figure 19

Fluorescence responses for varying oil injection rates in river bed sampling
using Prudhoe Bay oil. Tests at 1.0 ml/min and 0.236 ml/min oil rate show
oil stopped after an accumulation of 8.3 ml. and both show approximately the
same intensity after 60 min. The test run at 0.0236 ml/min also illustrates
the same intensity at 180 min. with an oil accumulation of 4.3 ml with the
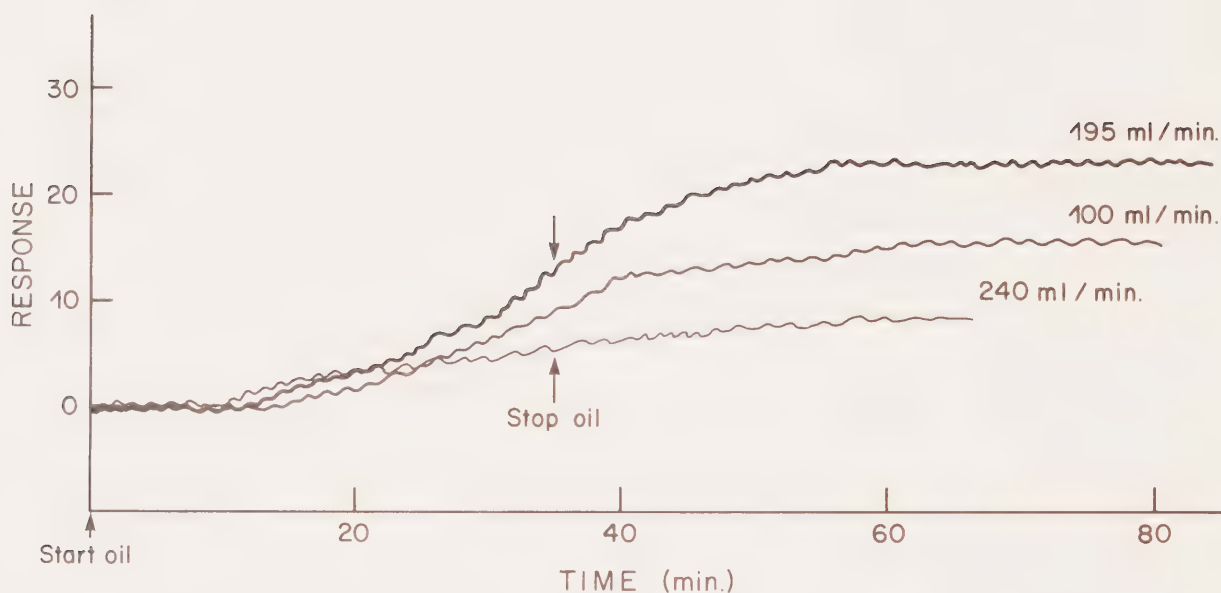oil still flowing. Notice the increasing time necessary to reach a response
of 4 units as the flow decreased.

Figure 20

Effect of changing flow rate of sampling in river
bed with Prudhoe Bay oil when sampler is 1 in.
downstream of oil source. This illustrates the fact
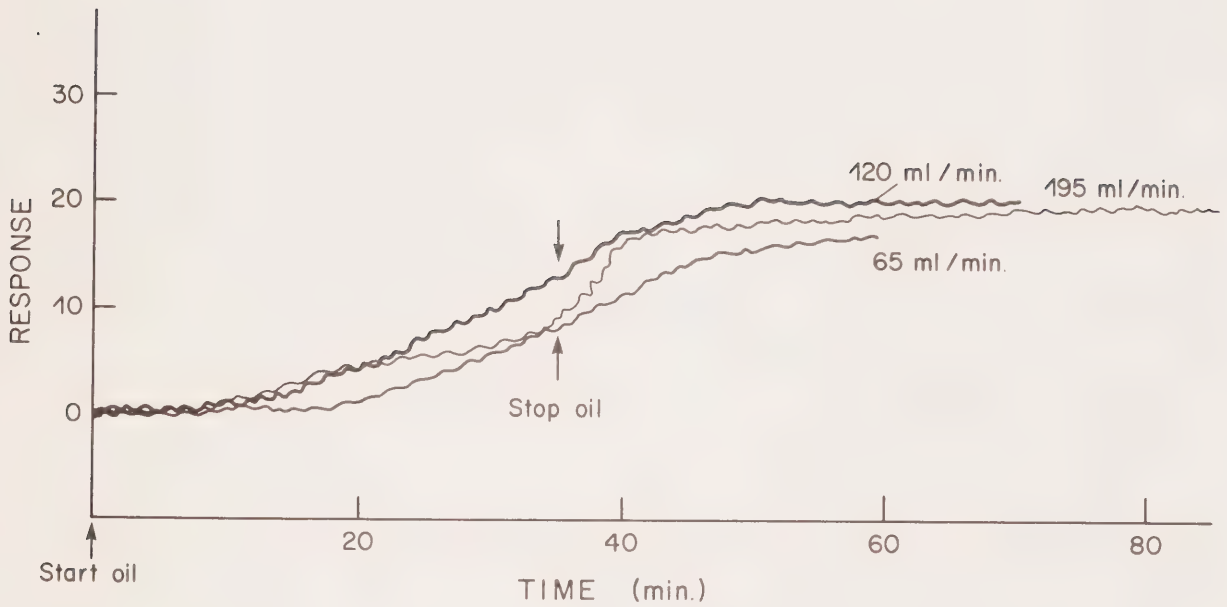that the highest flow rate yields the signal of lowest
intensity.

Figure 21

Effect of changing sampling flow rate in river bed
with Prudhoe Bay oil when sampler is above oil source.
Note that there is no great change in detection level
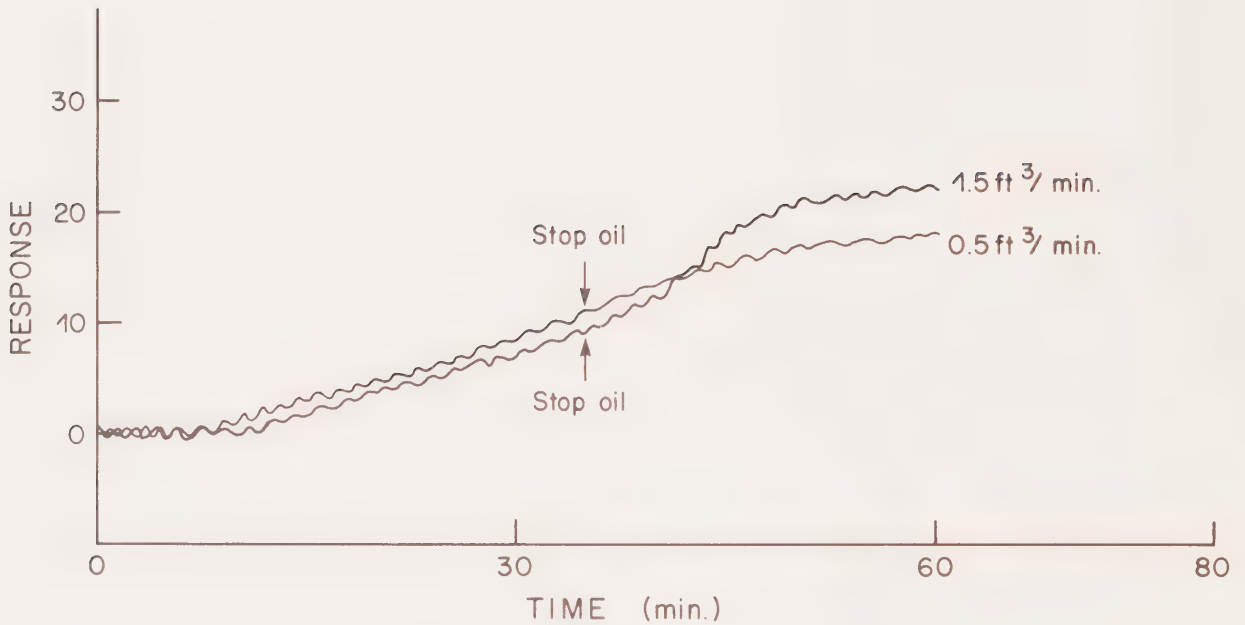with medium to low sampling flow rates.

Figure 22

Changing river water flow rate using a shallow sand
bed (2 in.) and Prudhoe Bay oil. Note there is
little affect in response to changing the flow rate
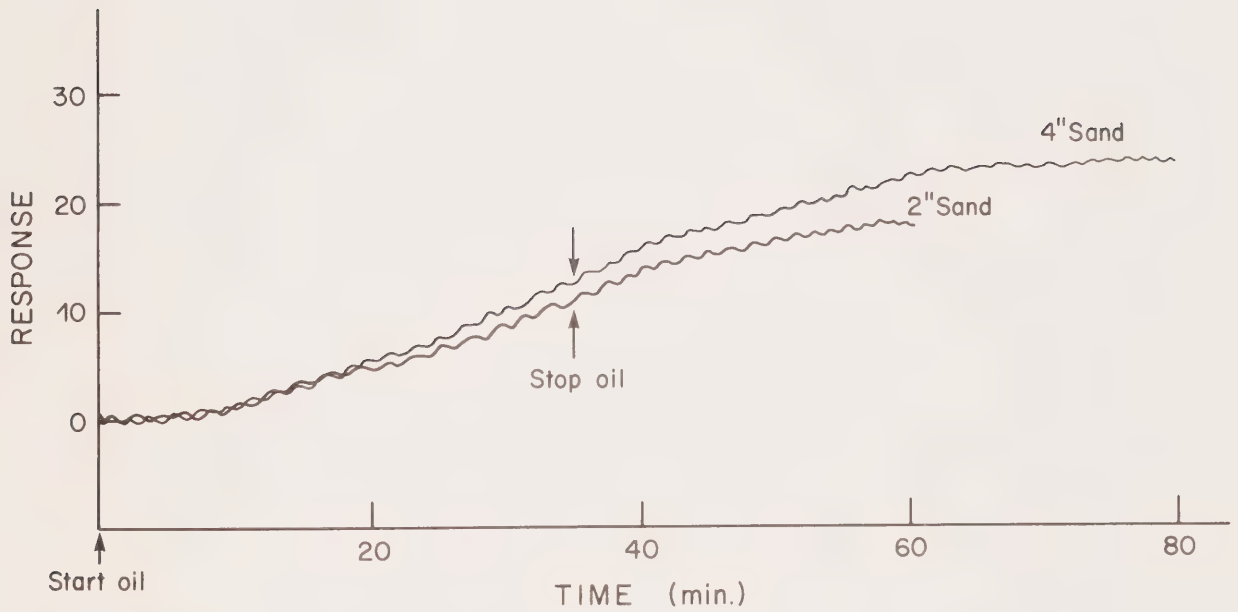from 0.5 ft³/min to 1.5 ft³/min.

Figure 23

Effect of changing sand depth above oil source using
Prudhoe Bay oil. Under similar conditions, plots
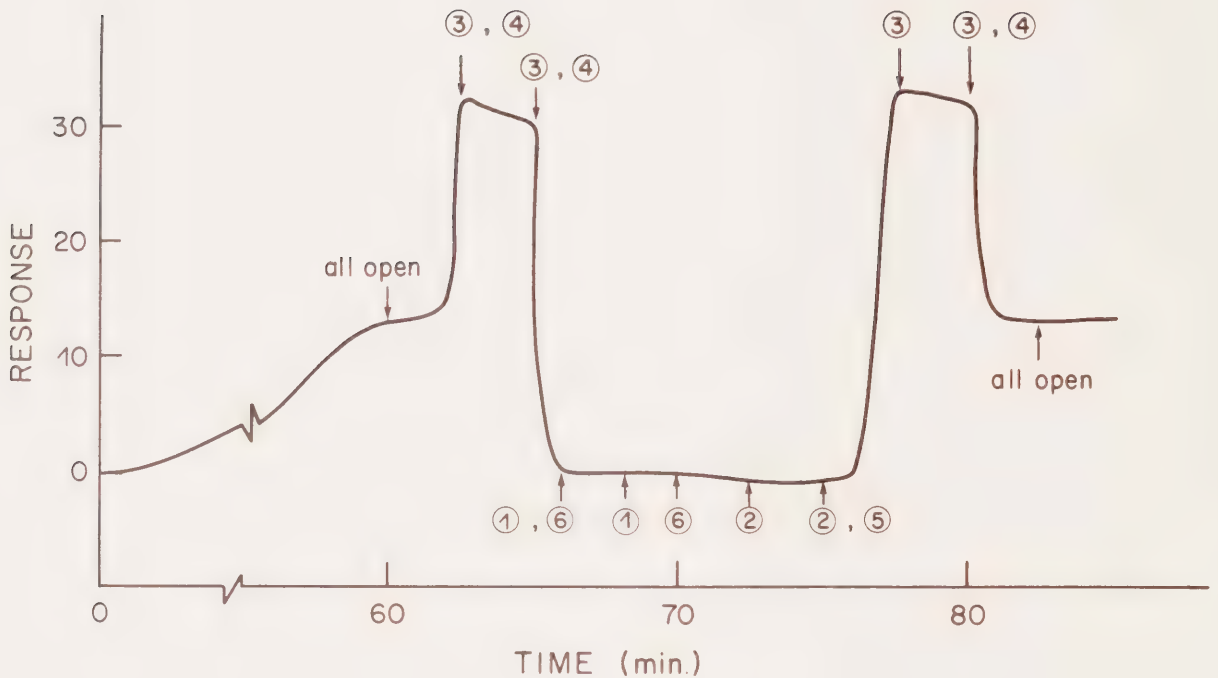for 2 in. and 4 in. show essentially no difference in
output.

Figure 24

Illustrates the effect of changing sampling positions
across the stream after oil was shut off and a plateau
level reached. Refer to Appendix B section 3 for
legend to numbered valves. Since oil injection took
place only at the central position the only positions
yielding responses were those of valves (3) and (4).
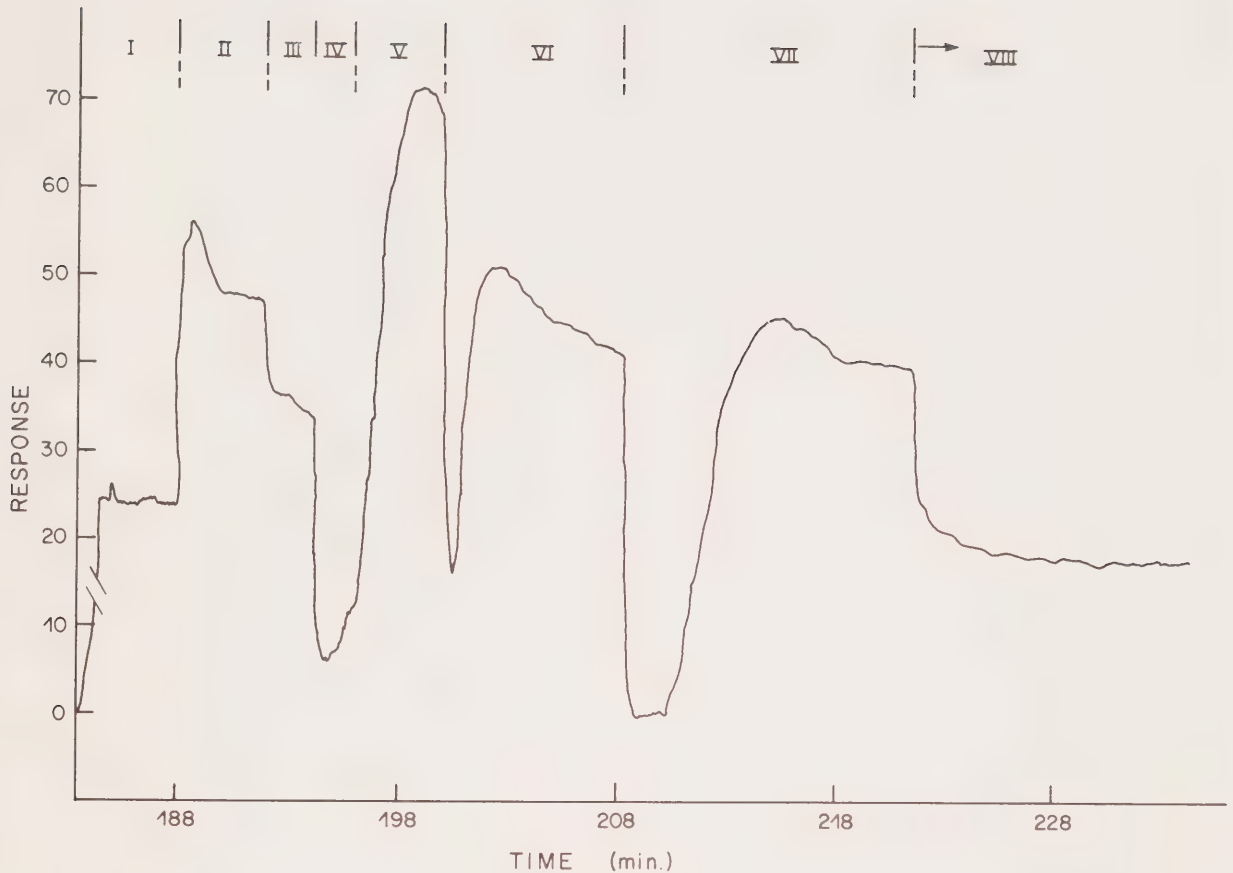For the indicated signals only 8.3 ml of oil had
entered the sand.

Figure 25

Effect of sampling through selected valves in a
sand-gravel river bed. After 166 min an
accumulation of 50 ml of oil had built up. This
test started at 186 min. with the pattern described
below. Refer to Appendix B section 3 for legend to
numbered valves. Valves indicated are valves open
in that region:

```
        I - (1)   (6)                V - (5)   (6)
       II - (1)   (2)   (6)          VI - (6)
      III - (1)   (2)   (5)   (6) VII - (1)
       IV - (1)   (5)   (6)        VIII - (1)   (6)
```
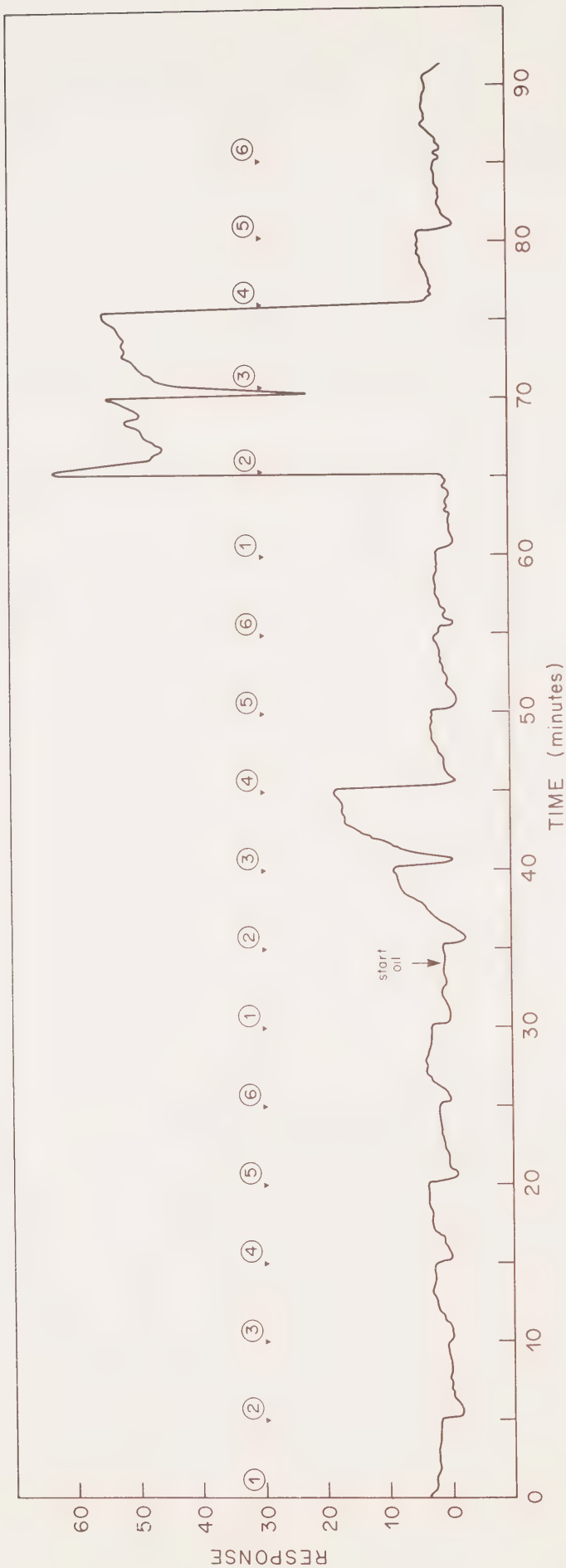
Figure 26

The effect of sequentially sampling the six intake frits of the ground bed sampling system for 5 minute durations is illustrated. The circled sequence of numbers indicate the intake frit open at that time and their location in the stream model may be verified by the legend in Appendix B Section 3. The oil was injected through a port bordered by intakes (2) and (3) at a time of 34 minutes and continued for the duration of the experiment. Note the immediate response from intakes (2) and (3) after 40 and 45 minutes and the much higher signal from the same frits after 70 and 75 minutes respectively.